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Benchmarking three-dimensional metal foam electrodes for the electrochemical reduction of nitrate

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23 **Abstract**

24 The electrochemical reduction of nitrate (ERN) is a promising and sustainable strategy for
25 addressing the critical issue of nitrate pollution in water sources. The rational design of
26 electrocatalysts has spotlighted metal-based three-dimensional (3D) electrodes such as Cu and Ni
27 foams. Metallic Cu foam showcases promising kinetics for ERN conversion, while Ni foam serves
28 as a robust support material for self-standing catalyst evaluation. This review underscores the
29 nuances and challenges in ERN research when exploiting 3D electrodes, emphasizing the
30 overlooked roles of pore per inch (*PPI*) and electrochemically active surface area (ECSA), as well
31 as the lack of standardization and inconsistent reporting practices, which hinders direct
32 performance comparison among different ERN studies. The *PPI* value controls reactant and
33 products mass transfer at the interface and impacts on the magnitude and extension of the solution
34 alkalization at the electrode surface, while ECSA is essential for accurately comparing the
35 specific electrocatalytic activity of metal foam electrodes for ERN. Particular attention is devoted
36 to modified self-standing 3D electrode materials, where the catalytic performance on either Cu or
37 Ni foams is altered by adding other metals and/or metal oxides ($\text{Cu}_{\text{foam}}/\text{M}$) and ($\text{Ni}_{\text{foam}}/\text{M}$),
38 respectively. A detailed analysis of selected modified Cu and Ni foam electrocatalysts available
39 in the literature is provided to demonstrate the lack of standardization reporting ERN performance
40 at present. Thus, we propose the adoption of more rigorous characterization and reporting
41 practices to advance the development of efficient and scalable ERN systems for sustainable water
42 treatment. This includes *PPI* value, ECSA determination and additional engineering figures of
43 merit encompassing both selectivity and conversion such as NH_3 generation efficiency (%) and
44 ERN energy efficiency (%). Parameters such as nitrate conversion, faradaic efficiency and
45 selectivity, often used as benchmarks, are considered not suitable enough for comparing different
46 ERN studies because they depend on the initial nitrate concentration, the total charge circulated
47 and the type of electrolysis (galvanostatic or potentiostatic).

48 **Keywords:** Nitrate reduction; Electrocatalysis; Cu foam; Ni foam; Benchmark; ECSA

49

50 1. Introduction

51 The never-ending search for water treatment alternatives to secure access to potable water
52 has advanced our understanding of technologies in the water-energy nexus [1,2]. Electrocatalysis
53 has been positioned as one of the most promising emerging sustainable technologies, transforming
54 pollutants into harmless compounds or added-value products without introducing extra chemicals
55 [3]. Electrified technologies use electrons to drive reactions of interest. Electrons are deemed
56 green chemicals when derived from renewable and clean sources of electricity. Therefore,
57 electrocatalysis offers appealing advantages compared to the conventional physical and
58 biochemical removal of pollutants [4,5].

59 Nitrate (NO_3^-) pollution is one of the top ten water quality violations worldwide [6,7].
60 The treatment of this challenging oxyanion is not trivial. Nitrate, as a ubiquitous contaminant, has
61 been treated by centralized large-scale methods such as reverse osmosis, ion exchange, and
62 bioremediation [8–11]. However, further treating brines and sludge from these approaches
63 increases operational costs by more than 30 % [12]. In this context, electrochemistry may open
64 new treatment avenues for sustainable management of nitrate pollution [13]. The electrochemical
65 reduction of nitrate (ERN) has two main goal products depending on the control on selective
66 transformation: nitrogen gas (N_2) and ammonia (NH_3). Product selectivity might be attained by
67 controlling specific experimental conditions, particularly the choice of electrode material utilized
68 [14–18] and the electrolyte composition [19,20]. For drinking water applications, the focus lies
69 on the obtention of harmless N_2 gas [21]. However, recent efforts have concentrated on producing
70 NH_3 as an added-value product [22,23] in line with ongoing efforts in the electrochemical
71 reduction of nitrogen [24,25]. This resource recovery approach has become a hot topic in
72 environmental research. Although this approach is in its infancy, the development of feasible
73 applications is becoming more achievable by incorporating NO_3^- pre-concentration systems, NO_3^-
74 conversion systems, and NH_3 recovery units.

75

76 Concerning NO_3^- electro-conversion systems, current research focuses on identifying
77 materials that exhibit high performance in NO_3^- conversion and demonstrate superior selectivity
78 toward NH_3 production [26–29]. While significant progress has been made in this aspect, fewer
79 studies have concentrated on scaling this process for real-world applications. To align this
80 approach on a large scale, several critical challenges must be addressed, including the utilization
81 of free-standing electrodes [30], stability against inorganic scaling produced in real water matrices
82 [31], designing suitable reactor configurations to maximize electrode utilization [32], and
83 achieving high NH_3 yield (measured in $\text{mmol NH}_3 \text{ g}^{-1}_{\text{cat}} \text{ h}^{-1}$ or $\text{mmol NH}_3 \text{ cm}^{-2}_{\text{cat}} \text{ h}^{-1}$) [33]. In
84 response to these essential requirements, open-pore metal foam electrodes have emerged as a
85 promising and viable configuration to overcome these challenges. Metallic foams offer various
86 advantages, including enhanced mass transport, excellent electrical conductivity, high
87 electrochemical surface area, and adaptability to different reactor configurations compared to
88 two-dimensional electrodes [34–36]. For instance, a comparison between Cu and Ni plate and
89 foam electrodes performance after an identical amount of charge transferred during ERN
90 electrolysis showed higher nitrate conversion (%), calculated using Equation 1, on Cu foam than
91 on plate, but almost identical values were reached on Ni foam and plate electrodes, as indicated
92 in Table 1.

$$\text{Nitrate conversion (\%)} = \frac{C_{\text{NO}_3^-,0}}{C_{\text{NO}_3^-,0} - C_{\text{NO}_3^-,t}} \times 100 \quad (1)$$

93 where $C_{\text{NO}_3^-,0}$ is the initial nitrate concentration ($\text{mg NO}_3^- \text{-N L}^{-1}$), and $C_{\text{NO}_3^-,t}$ is the nitrate
94 concentration at time t ($\text{mg NO}_3^- \text{-N L}^{-1}$).

95 Thus, the role of metal foams during the ERN may vary depending on their composition,
96 which influences their characterization and activity evaluation. Metal foam applied for ERN can
97 be classified into three types: *i*) active materials (such as Cu foam), *ii*) support materials (inactive
98 current collectors, like Ni foam), and *iii*) modified materials (catalyst-supported electrodes, where
99 foam electrodes—whether active or inactive—are fully or partially coated with an additional
100 catalytic material, denoted as $\text{Cu}_{\text{foam}}/\text{M}$ and $\text{Ni}_{\text{foam}}/\text{M}$, respectively).

101 **Table 1.** Comparison of ERN galvanostatic electrolysis results on Cu and Ni electrodes using
 102 plate and foam electrodes. Plate electrodes were evaluated at 20 mA cm⁻² during 90 min on 6.0
 103 cm² electrodes (Q = 648 C). Initial solution composition: 100 mg L⁻¹ NO₃⁻-N in 50 mM Na₂SO₄.
 104 Foam electrodes were evaluated at 40 mA cm⁻² during 120 min on 2.25 cm² electrodes (Q = 648
 105 C). Initial solution composition: 30 mg L⁻¹ NO₃⁻-N in 12.5 mM Na₂SO₄.

Element	Electrode	Nitrate Conversion
	Configuration	(%)
Cu	Plate [37]	22 ± 2
	Foam [38]	55 ± 4
Ni	Plate [37]	8 ± 2
	Foam [39]	10 ± 2

106

107 Independently of the initial pH solution, the ERN mechanism yields hydroxide ions that
 108 increase solution pH, reaching in some instances values as high as pH 11. The solution
 109 alkalization during ERN promotes the generation of oxides and hydroxides on the metallic
 110 electrode surface. Consequently, the coexistence of metal, oxide, and hydroxide sites on the foam
 111 electrode surface increases entropy and facilitates the provision of adsorption sites during ERN.
 112 Table 2 provides a summary of the bulk resistivity of various materials, including C, Ni, Cu, Cu-
 113 based oxides, Ni-based oxides, Al₂O₃, and SiO₂. These values underscore the exceptional
 114 electrical conductivity of Cu and Ni foams and exhibit much lower bulk resistivity (Ω cm) for
 115 passive Cu and Ni-based oxides than for insulating-type oxides such as Al₂O₃ and SiO₂. Therefore,
 116 the presence of Cu- and Ni-based oxides on the foam surface does not significantly impact the
 117 overall conductivity of the electrode. On the contrary, the presence of these oxides in small
 118 quantities can be advantageous for increasing the overall electrochemically active surface area
 119 (ECSA), number of adsorption sites, and electrode stability [40]. In fact, some studies suggest
 120 that these metal oxides may have higher electrocatalytic activity on the reduction of oxyanions
 121 [41–43].

122 **Table 2.** Bulk resistivity (Ω cm) of various materials considered as conductors, semiconductors,
 123 and insulators.

Material	Bulk resistivity (Ω cm)
Carbon foam*	32.3×10^{-2}
Nickel foam**	6.9×10^{-6}
Cu foam*	65.2×10^{-6}
Cu_2O [44]	3.7×10^3
CuO[44]	1.1×10^3
NiO_x [45]	$1.0 \times 10^2 - 1.0 \times 10^9$
$\text{Ni}(\text{OH})_x$ [46]	$1.0 \times 10^5 - 1.0 \times 10^6$
Al_2O_3 [47]	$1.0 \times 10^{15} - 1.0 \times 10^{17}$
SiO_2 [47]	$1.0 \times 10^{14} - 1.0 \times 10^{16}$

124 *Values provided from the manufacturer: ERG Aerospace Corporation

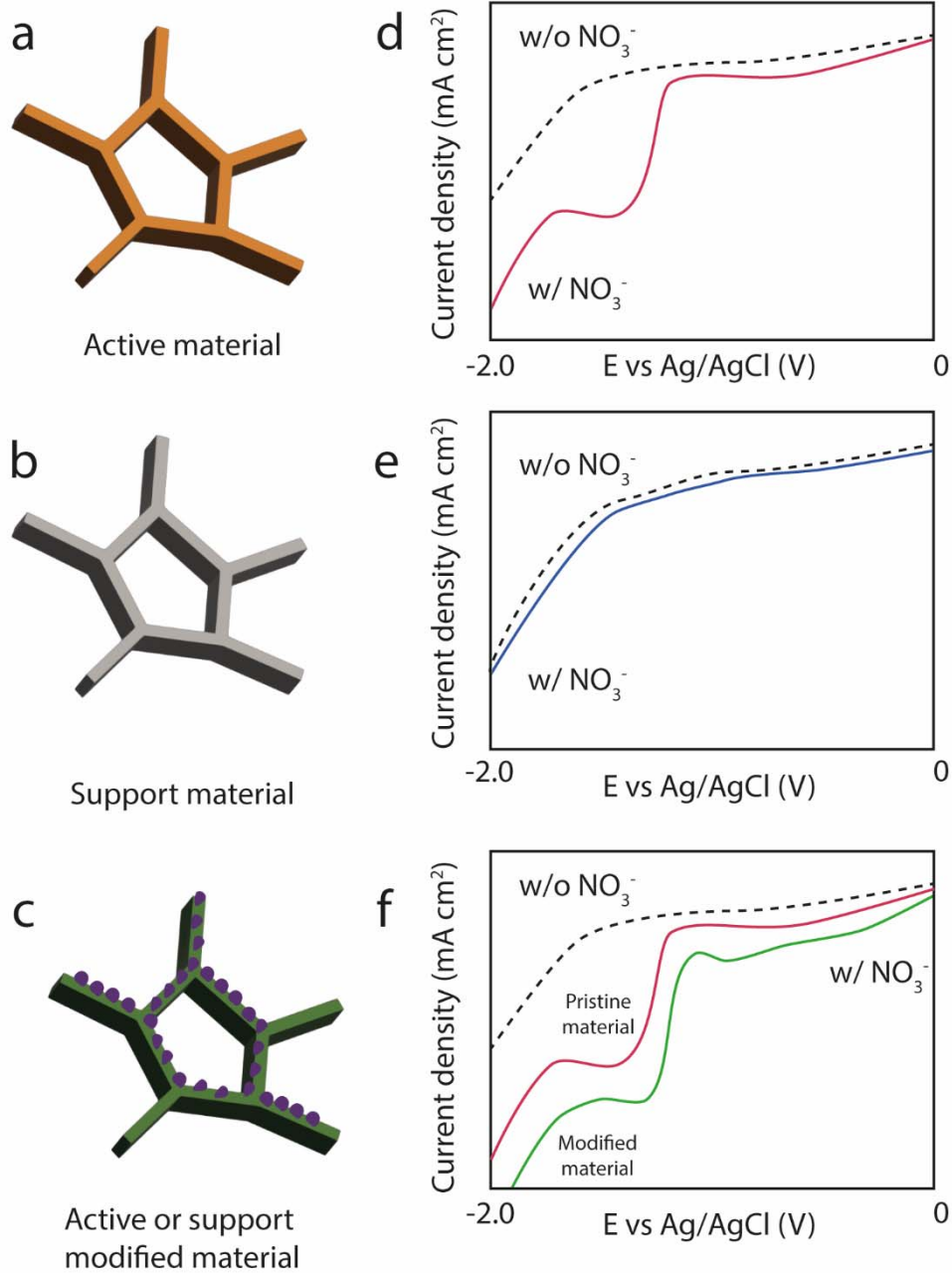
125 **Values provided from the manufacturer: ATT Advanced elemental materials

126 This critical review delves into the fundamental parameters of three-dimensional (3D)
 127 foam electrodes and underscores the importance of accurate interpretation for reporting ERN
 128 performance. It looks into the multifaceted role of metal foams, exploring its functionality as an
 129 active material, support material, and modified foam. The review encompasses pertinent
 130 examples of 3D modified electrodes aimed at enhancing electrocatalytic performance in ERN,
 131 along with a discussion of the most recent modification strategies. By presenting these materials,
 132 the review offers an updated overview of the current state-of-the-art in this specialized research
 133 domain. Furthermore, the review extends its perspective to the future by outlining potential
 134 directions and identifying gaps that require attention for the further development of 3D foam-
 135 based electrocatalysts in ERN applications.

136

137 **2. Defining key characterization parameters of metal-based three-dimensional foam**
138 **electrodes**

139 Considering their distinctive features, 3D metal foam electrodes (e.g., Cu, Ni, Co, Al)
140 have emerged as the primary substrate or active material for electrocatalysis in many fields [48–
141 50]. The 3D configuration provides excellent electrical properties and a smart spatial
142 configuration that results in outstanding ERN performance. The choice of conductive material
143 depends on the role of the electrode during the ERN, which may be a support electrode, active
144 electrode, or both [51–53]. This classification is determined by the electrocatalytic response of
145 the pristine foams and modified materials in the presence of NO_3^- , as evidenced by the increase
146 in current density, as illustrated in Figure 1. The most determining properties to characterize in
147 these materials are pore per inch (*PPI*) and electrochemically active surface area (ECSA). These
148 physical descriptors play a relevant impact in catalytic activity evaluation as they drive the
149 comparisons in terms of mass transfer efficiency and applied current density (j , mA cm^{-2}),
150 respectively.



151

152 **Figure 1.** Classification of foam electrode: (a) active material, (b) support material, and (c) active
 153 or support modified material. Linear sweep voltammetry of (d) Cu_{foam} , (e) Ni_{foam} , and (f)
 154 $\text{Cu}_{\text{foam}}/\text{Co}(\text{OH})_x$ conducted in Na_2SO_4 solution in absence and presence of NaNO_3 at 50 mV s^{-1} .
 155 Adapted from [17,38,39].

156

157

2.1 On the relevance of emptiness: describing pore per inch (PPI)

The *PPI* is a commonly overlooked but crucial parameter to characterize metal foam materials. The *PPI* refers to the number of pores present per linear inch of the foam structure, giving a direct average value of emptiness contained in the 3D structure [54]. The number of pores can indirectly indicate average pore size/diameter since smaller pores can be encapsulated with a higher density in a linear inch. Thus, higher *PPI* values are generally associated with notoriously smaller pore sizes and less efficient mass transfer. Therefore, the *PPI* value is essential for the possible implementation of 3D foam electrodes in flow-through and flow-by electrochemical reactor designs, as it controls the hydrodynamic behavior of solution flowing through the interconnected pores in the foam [55,56]. For instance, the electrochemical characterization of reactors (flow-through and flow-by) can be performed using the volumetric mass transport coefficient ($k_m A$) for a process controlled by mass transfer. This parameter, typically evaluated using the limiting current from a monoelectronic redox mediator in solution such as ferrocyanide ion over various electrolyte mean linear flow velocities, provides both mass transfer coefficient (k_m , m s^{-1}) and electroactive specific area (A_s , m^{-1}) properties in flow-by reactors [57–62]. The $k_m A$ (s^{-1}) is determined from the limiting current I_L (A) according to Equation (2)

$$k_m A_s = \frac{I_L}{nFCV_c} \quad (2)$$

where n is the number of electrons involved in the reaction ($n = 1$, considering the redox couple $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$), F is the Faraday's constant (96485 C mol^{-1}), C is the bulk concentration of $\text{Fe}(\text{CN})_6^{3-}$ (mol m^{-3}), and V_c is the active volume (m^3).

On the other hand, flow-through reactors can be also characterized using the $k_m A$ vs. I_L relationship, according to Equation (3)

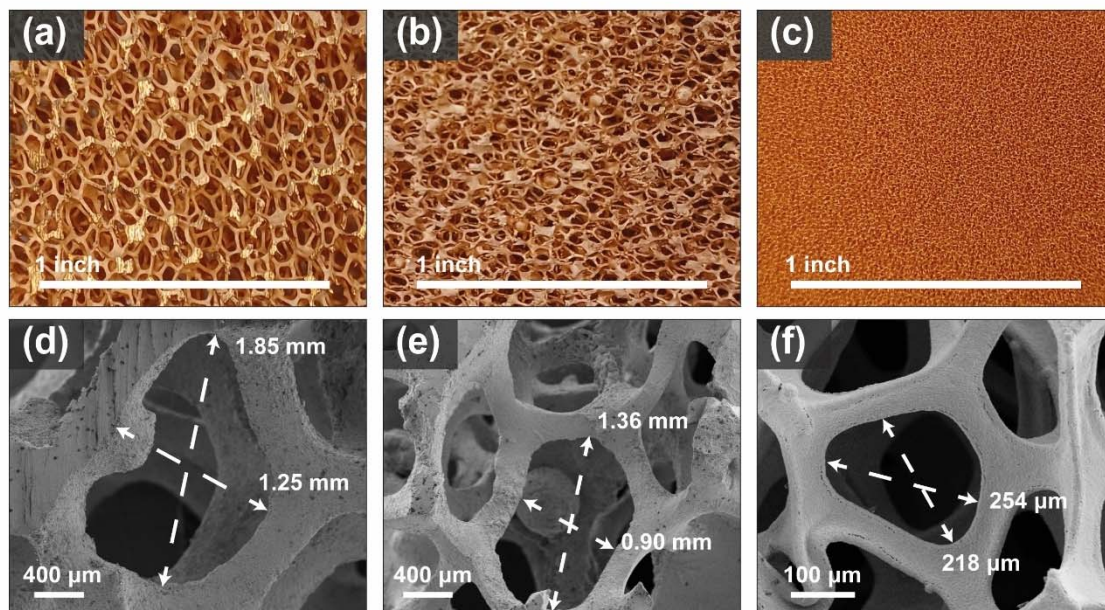
$$I_L = nFCuA_r \left[1 - e^{\left(\frac{-Lk_m A_s}{u} \right)} \right] \quad (3)$$

180 where n is the number of electrons involved in the electrochemical reaction, u is the flow rate (m
181 s^{-1}), A_r is the cross-sectional area (m^2), and L is the thickness of the porous electrode (m) [63,64].

182 Figure 2 illustrates three Cu foams with increasing PPI s of 20, 40, and 110. The optical
183 images (Figures 2a, b, and c) clearly illustrate the polydisperse nature of interconnected pores and
184 the decreasing pore size distribution with increasing PPI number. Figures 2d, e, and f illustrate
185 the heterogeneous morphology of the pores by scanning electron microscope (SEM) at low
186 magnification (74X) and 5 keV. It can be observed that the average diameter of interconnected
187 pores decreases in size with increasing PPI , going from an average value of 1.55 mm at 20 PPI
188 down to 236 μm at 110 PPI .

189 In porous structures such as 3D metal foams, surface area (cm^2) can be normalized in two
190 distinct ways. Firstly, by areal density, which is related to the mass or amount of material ($cm^2 g^{-1}$).
191 Secondly, the specific surface area (SSA) is expressed relative to the volume of the 3D foam
192 ($cm^2 cm^{-3}$). Both parameters hold particular significance in electrocatalysis, where processes are
193 primarily driven by interfacial interactions. Notably, both areal density and SSA exhibit a linear
194 increase with rising PPI .

195 Furthermore, the inherent tortuosity of foams with varying PPI significantly affects reactants
196 and product mass transfer close to the foam surface. Higher PPI values lead to increased
197 tortuosity, impacting the renewal of reactant from the bulk solution and the accumulation of
198 products at the electrode surface. Conversely, lower PPI values can enhance mass transfer by
199 facilitating concentration equilibrium between interfacial and bulk solution species [65,66]. In
200 particular, the interfacial pH can drastically increase during ERN and differ from the bulk solution
201 pH depending on operational conditions. Thus, the PPI value impacts the magnitude and
202 extension of the solution alkalization at the electrode surface. Subsequently, the local alkaline
203 pH can exacerbate additional issues in complex water matrices due to Mg^{2+} and Ca^{2+} ions,
204 resulting in inorganic scaling on the foam surface [31,67]. Consequently, different PPI values
205 may influence the decrease in ERN activity on the foam due to inorganic scaling on the electrode
206 surface.



207

208 **Figure 2.** Cu foam at 20, 40, and 110 PPI at different conditions: (a, b, c) optical imaging, and
 209 (d, e, f) SEM images to determine surface morphology. Cu foam 20 and 40 PPI were acquired
 210 from ERG Aerospace Corporation and 110 PPI from Futt.

211 **2.2 The interconnection of electrocatalytic response and the electrochemically**
 212 **active surface area (ECSA)**

213 For applications in electrocatalysis, the reactive surface area is one of the most important
 214 parameters. In the case of 3D metal foams, the actual electroactive surface area is significantly
 215 different from the geometrical area. Thus, the specific surface area of a foam is the amount of
 216 surface area within a given bulk volume of foam. Consequently, various methods have been
 217 employed to estimate this relevant parameter. One commonly used technique for surface area
 218 measurement in catalyst's characterization is the gas adsorption, which is based on argon (Ar),
 219 krypton (Kr) or nitrogen (N₂) gas physisorption on the solid catalyst at cryogenic temperature by
 220 the Brunauer-Emmett-Teller (BET) approach [68,69]. However, this *ex-situ* technique faces
 221 challenges when examining samples that are predominantly macroporous (i.e., metal foams with
 222 low PPI) with a lower surface area in comparison with meso- and micro- porous materials (e.g.,
 223 zeolites, activated carbons, and metal organic frameworks (MOFs)). Notably, metal foam
 224 electrodes typically represent low surface area samples (<1 m²/g), rendering N₂ physisorption

225 unsuitable for most cases. Alternatively, Kr physisorption at 77 K has been successfully employed
226 for evaluating surface area in metal foam electrodes [70]. Furthermore, mercury porosimetry has
227 proposed as an alternative approach to assess the size distribution and porosity of metal-based 3D
228 electrodes [71]. Giving that metal foam electrodes operate within an electrochemical solid/liquid
229 interface during ERN, estimating and comparing their ECSA, which may not necessary equivalent
230 to the total surface area estimated by gas physisorption or other physical methods [51], represents
231 a major point of attention to benchmark different studies.

232 The ECSA denotes the active surface area actually involved in the electrochemical process
233 [40,51,72,73]. The larger the ECSA, the greater the number of active sites available for
234 electrochemical reactions to occur, leading to enhanced reaction rates and improved efficiency in
235 a shorter treatment time. Although 3D metal foam electrode substrates can play different roles
236 (i.e., active material, support material, or modified material), the ECSA can be evaluated
237 regardless of that role. Thus, different single or multi-component foam-based materials can be
238 benchmarked as electrocatalysts by normalizing their electrochemical response via their
239 corresponding ECSA. The ECSA should be determined for the actual electrode under study since
240 the bare metal foam electrodes might either diminish or increase their ECSA after incorporating
241 an additional catalytic material on top.

242 Although multiple methods have been suggested for determining ECSA [72], discrepancies
243 and errors persist in electrocatalyst research and make the present discussion timely. A common
244 flaw is the misuse of the Randles-Sevcik equation to evaluate the ECSA for 3D materials.
245 Randles-Sevcik relies on the use of an outer-sphere redox mediator in solution (*i.e.* $K_3Fe(CN)_6$)
246 to estimate ECSA. However, Randles-Sevcik is not applicable to the case of metal foam electrodes
247 since this approach is only strictly pertinent for evaluating planar electrodes or those with semi-
248 infinite diffusion [74]. Hence, when used to determine the ECSA of 3D materials, the results are
249 unreliable and mainly correspond to the 2D geometric surface area evaluation.

250 The ECSA of 3D metal foam electrodes can be estimated instead from the double layer
251 capacitance (C_{dl}) and the specific capacitance (C_s) values, according to Equation (4):

$$ECSA (cm^2) = \frac{C_{dl}}{C_s} \quad (4)$$

252 where C_{dl} represents the double layer capacitance (μF) obtained either from cyclic voltammetry
253 (CV) or electrochemical impedance spectroscopy (EIS); and C_s the specific capacitance value (μF
254 cm^{-2}). The C_s is generally defined for an ideal flat surface and depends on the nature of the catalyst
255 (metal or metal oxide), as well as the solution pH (alkaline or acid). Different C_s values can be
256 found in the literature in the range from 20 to 80 $\mu\text{F cm}^{-2}$ [51,75], being in most cases around 40
257 $\mu\text{F cm}^{-2}$ for both Ni and Cu oxide in alkaline solution [40,51,73,75] and 20 $\mu\text{F cm}^{-2}$ for the case
258 of metallic Ni in alkaline solution [36]. Thus, ECSA comparison is only possible between similar
259 electrocatalysts evaluated under similar experimental conditions [72], which is the case of
260 comparing bare metal foam electrodes (Cu or Ni foams) and multi-component foam-based
261 electrodes ($\text{Cu}_{\text{foam}}/\text{M}$ or $\text{Ni}_{\text{foam}}/\text{M}$ electrodes) during ERN. Nevertheless, ECSA estimation
262 contains a significant range of uncertainty due to the wide dispersion in C_s values. The use of
263 Equation (4) it is useful mainly for comparison purposes and not for obtaining absolute values
264 [72].

265 The formation of an electrical double layer (EDL) at the electrode-electrolyte interface is a
266 fundamental phenomenon in electrochemistry [76,77]. When an electrode is immersed in an
267 electrolyte solution, ions from the solution are attracted to the electrode surface due to electrostatic
268 forces. This phenomenon results in the formation of two layers of charge: one layer of ions
269 adsorbed onto the electrode surface (the inner Helmholtz plane) and another layer of oppositely
270 charged ions in the solution adjacent to the electrode surface (the outer Helmholtz plane). Under
271 the assumption that no Faradaic processes take place within this narrow potential range (i.e., no
272 electron transfer reactions involving redox electroactive species), the behavior of the double layer
273 resembles that of a capacitor. In other words, the electrode-electrolyte interface defined by the
274 double layer behaves like a capacitor. Consequently, the estimated C_{dl} is directly connected to the
275 ECSA, since an extended surface area facilitates increased ion adsorption, thus amplifying the
276 electrical double layer and its capacitance. The most common electrochemical approach to
277 estimate the C_{dl} is based on capacitive current evaluation by CV as a function of scan rate in a

278 narrow non-Faradaic potential range, using Equation (5), which assumes an ideal capacitor
279 behavior [78].

$$C_{dl} = \frac{\Delta I / 2}{\nu} \quad (5)$$

280 where $\Delta I/2$ (A) denotes the half-current difference between the anodic and cathodic currents at
281 central potential, and ν stands for the scan rate (V s^{-1}). The slope from the corresponding graphical
282 representation provides the C_{dl} value.

283 Despite the seemingly direct calculation of ECSA from CV, the procedure requires
284 meticulous care. Several factors need consideration to obtain accurate C_{dl} values, even for flat 2D
285 electrodes. For the case of 3D metal foam-based electrodes, the task becomes more complicated.
286 Essential aspects to be considered during the electroanalytical procedure include but are not
287 limited to the electrical connections, effects of trapped air, electrode wettability, and surface
288 tension. Note that several of these aspects are *PPI*-dependent. As reported by Morales *et. al*
289 several steps should be considered in order to obtain reliable ECSA values [79]. Figure 3 details
290 four main steps and electrochemical considerations essential for obtaining ECSA comparison
291 among electrocatalysts.

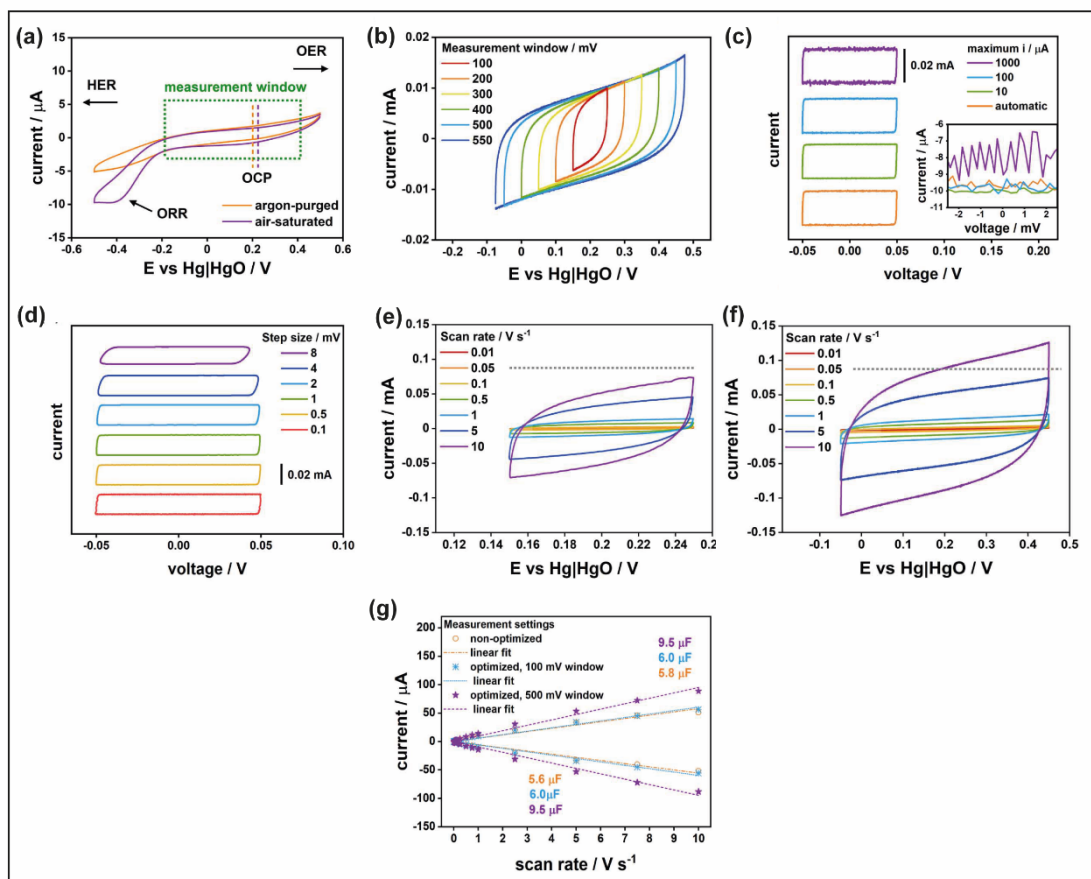
292 Step 1: Initially it is crucial to perform CV scans over a wide potential range to identify
293 regions where non-Faradaic current dominates and there is an absence of peaks or evidence of
294 Faradaic current. Neglecting this step could lead to an inaccurate depiction of capacitor
295 characteristics. As presented in Figure 3a, the non-Faradic region (enclosed by the green dotted
296 square) can be identified in the wide potential range. It is important to recognize that the specific
297 range varies based on the material electrochemical properties. Thus, it should be estimated in each
298 individual case. While many studies typically employ the open circuit potential (OCP) value as
299 the central potential, this approach is not universally applicable. For example, Cu foam presents
300 a Faradaic oxidation process in close proximity to the OCP in $0.1 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ [17]. Moreover,
301 when defining the range, it is essential to ensure that both cathodic and anodic currents overlap
302 in two subsequent potential scans, typically conducted within a window of 100 and 500 mV (see

303 Figure 3b). This overlapping also depends on the electrode material and the scanned potential
304 range.

305 Step 2: Researchers should optimize the data collection parameters since calculated
306 capacitance values are sensitive to variations of these parameters. While recording CV at different
307 scan rates, it is crucial for the operator to consider parameters such as current range and the size
308 of voltage step. Although the current range can be set either automatically or manually, it may
309 vary over several orders of magnitude depending on the range of scan rates employed. It is
310 advisable to assess the noise in the measurement by comparing results obtained at different current
311 range limits as presented in Figure 3c. An improper selection of the current range can introduce
312 significant noise into the measurements. Therefore, conducting separate experiments for each
313 scan rate, rather than using the same current range across both fast and slow scan rate, can be
314 beneficial. Additionally, careful selection of the voltage step size is essential, especially when
315 evaluations are carried out over a small range of 100 mV. Figure 3d shows the effect of choosing
316 an unsuitable voltage step on the data collection during the assessment. The voltage step affects
317 the CV profile near the upper and lower set potentials.

318 Step 3: Once the optimal data collection parameters have been identified, measurements
319 should be carried out spanning a broad range of scan rates (i.e., from 500 to 5 mV s^{-1}). While
320 higher scan rates might be applicable depending on the material being evaluated, slower rates can
321 be time-consuming and may not provide significant information about capacitance of the system.
322 Therefore, it is recommended to perform evaluations within the range of 250 to 5 mV s^{-1} when
323 working with metal foams. Figure 3e presents a CV evaluation without considering the optimal
324 conditions, while Figure 3f denotes the CV performed at optimal conditions. Comparing both
325 graphs, a current underestimation was produced when the CV conditions were not optimized. The
326 improperly optimized parameters result in a CV profile with sharpened extremes, current noise,
327 and lower current compared to the reference dotted line. Conversely, under optimized parameters,
328 the CV profiles exhibit well-defined extremes, no evidence of noise within the selected current
329 range, and higher current compared to the same reference dotted line.

330 Step 4 - Once the data are collected, the analysis can be undertaken by considering the
 331 cathodic current intensity, anodic current intensity, or the average of these two currents. The
 332 capacitance values are calculated as mentioned, using Equations (4) and (5). Figure 3g presents a
 333 comparison of capacitance values calculated using non-optimized and optimized conditions at
 334 different potential ranges. It is noteworthy that under non-optimized conditions, the calculated
 335 capacitance underestimates the system capacitance, whereas under optimized conditions, the
 336 capacitance is 1.6 times higher than non-optimized conditions. Hence, determining the ECSA
 337 appropriately is crucial for comparing electrocatalysts. It is important to realize that each material
 338 requires unique conditions, and ECSA should be reported by the most appropriate evaluation.



339
 340 **Figure 3.** (a) Cyclic voltammetry of an electrochemical cell at 10 mV s^{-1} to identify measurement
 341 window. (b) Cyclic voltammetry at 500 mV s^{-1} considering different measurement windows. (c)
 342 Resistor-capacitor circuit evaluated at different maximum current parameter values and (d)
 343 evaluation of the step size in the data collection RC-circuit. Evaluation of ECSA by CVs under

344 (e) non-optimized and (f) optimized electrochemical parameters. (g) Capacitance values obtained
345 under different conditions. All measurements were performed in an argon-purged 0.1 mol L⁻¹
346 NaOH aqueous solution. Figures adapted from [79] (CC-BY 4.0 - IOP Publishing).

347 The EIS is an alternative electroanalytical technique to estimate ECSA from C_{dl} . In particular,
348 EIS exhibiting capacitive current in the high frequency domain allows to evaluate the interfacial
349 capacitance. The interfacial capacitance simultaneously embraces the C_{dl} contribution and the
350 capacitance associated with the oxide and/or hydroxide layer formed on some metallic surfaces
351 during ERN. This inclusion is relevant in the case of metallic foams such as Cu and Ni, as it is
352 commonly reported the formation of oxide/hydroxide layers. This type of complex metal-oxide-
353 electrolyte interface is not fully described by an ideal capacitor behavior and requires the use of
354 a constant phase element (CPE). The CPE is a mathematical element that helps to fit the
355 equivalent circuit and account for the distribution of dielectric properties of the interface [78].
356 Typically, after EIS assessment at potentials on the capacitive current domain in a frequency range
357 from 100 kHz to 0.01 Hz, either graphical analysis is performed [80] or an equivalent circuit is
358 modeled and fitted to the EIS data after solution resistance (R_s) correction. The simplest and most
359 common equivalent circuit involves the R_s , the charge transfer resistance (R_{ct}), and a CPE
360 representing the double layer capacitance. The frequency-dependent impedance (Z) for a CPE is
361 defined by Equation (6).

$$Z_{(\omega)} = \frac{1}{Q(i\omega)^\alpha} \quad (6)$$

362 where Z is the impedance in $\Omega \text{ cm}^{-2}$, i is the imaginary part of the complex number, and ω the
363 angular frequency in rad s^{-1} . The parameters related to the CPE are Q and α ($1 \geq \alpha \geq 0$), which are
364 determined from the equivalent circuit fitting and are independent of the frequency. If $\alpha = 1$ the
365 CPE is a capacitor and Q is the C_{dl} and if $\alpha = 0$ the CPE is a resistor and Q is the resistance.
366 Meanwhile, the C_{dl} when $\alpha \neq 1$ and ≥ 0.7 can be estimated by Equation (7) [81,82].

$$C_{dl} = \left[Q \left(\frac{1}{R_s} + \frac{1}{R_{ct}} \right)^{\alpha-1} \right]^{1/\alpha} \quad (7)$$

367 Various studies in the literature have compared ECSA values ascertained from CV and EIS,
368 attempting to gauge the accuracy of each technique given significant differences that oscillate
369 between $\pm 15\%$ and $\pm 40\%$ [40,75,79,82,83]. In studies evaluating different electrode
370 compositions or modified materials, both CV and/or EIS can be applicable without preference, if
371 comparison is conducted under similar experimental conditions. Regarding equipment
372 capabilities, the CV approach is basic and simpler compared to EIS, which requires a specific
373 module and further specialized data treatment. However, a comprehensive evaluation of 3D foam-
374 based electrodes is still lacking, leaving unresolved the question of the preferred method in such
375 scenarios.

376 Estimating the ECSA is an important step to benchmark electrocatalytic performance of 3D
377 electrodes. The ECSA and the *PPI* value play a relevant role to ascertain an accurate activity
378 evaluation under identically comparable current density. In order to enable direct benchmarking
379 of electrocatalysts for ERN, authors should provide reliable metrics normalized by the
380 electroactive area of the material in consideration. When considering the NH_3 yield from ERN,
381 outcomes are barely reported in intrinsically comparable intensive metrics. A few articles that
382 encompass the use of such relevant metrics for direct benchmarking report drastically different
383 key indicator parameters such as the catalytic activity per mass or the catalytic activity per surface
384 area. It is important to remark that in the case of 3D foam-based electrodes, where the mass of the
385 active material might be difficult to estimate, the intrinsic electrocatalytic activity normalized and
386 compared using the ECSA seems to be a more suitable approach to enable transparent and direct
387 comparison between electrocatalyst development outcomes in literature. While the ECSA can be
388 used for comparison between electrocatalyst, the use of 3D metal foam in flow-through or flow-
389 by reactors for ERN under mass transfer conditions should be evaluated using the $k_m A$ parameter
390 to account for dimensional and structural differences between electrode configurations [63]. By
391 combining the ECSA or the geometrical 3D area, the mass transfer coefficient can be estimated
392 and compared between the two area determination approaches. Comparisons between electrodes

393 with different PPI values should be performed under the same hydrodynamic pattern (flow-
394 through or flow-by reactors) to clearly establish the benefits on mass transfer parameters.

395 **3. Understanding differences between scaffolds and active supports: Selected examples** 396 **of novel modified foam-based electrocatalysts for ERN ($\text{Cu}_{\text{foam}}/\text{M}$ and $\text{Ni}_{\text{foam}}/\text{M}$)**

397 The rational design of electrocatalysts often prioritizes the use of earth-abundant materials,
398 either in bulk or nano-enabled configurations, to minimize electrode capital costs. While platinum
399 group materials (PGMs) are well-known for their exceptional catalytic performance, their high
400 cost and scarcity limit their usage to ultra-low content or single-atom configurations [37,84].
401 Consequently, most bulk metal-based 3D electrodes discussed in the literature predominantly
402 feature earth-abundant metals such as Cu and Ni. The mechanisms and fundamentals of ERN on
403 those materials have been thoroughly discussed in several review articles [14,85–87]. In contrast,
404 the benchmarking of ERN based on robust self-standing Cu- and Ni-based electrodes has been
405 seldom explored. Thus, this section reviews some selected studies from the literature that used
406 either active or scaffold modified materials ($\text{Cu}_{\text{foam}}/\text{M}$ and $\text{Ni}_{\text{foam}}/\text{M}$) as electrodes for the ERN.

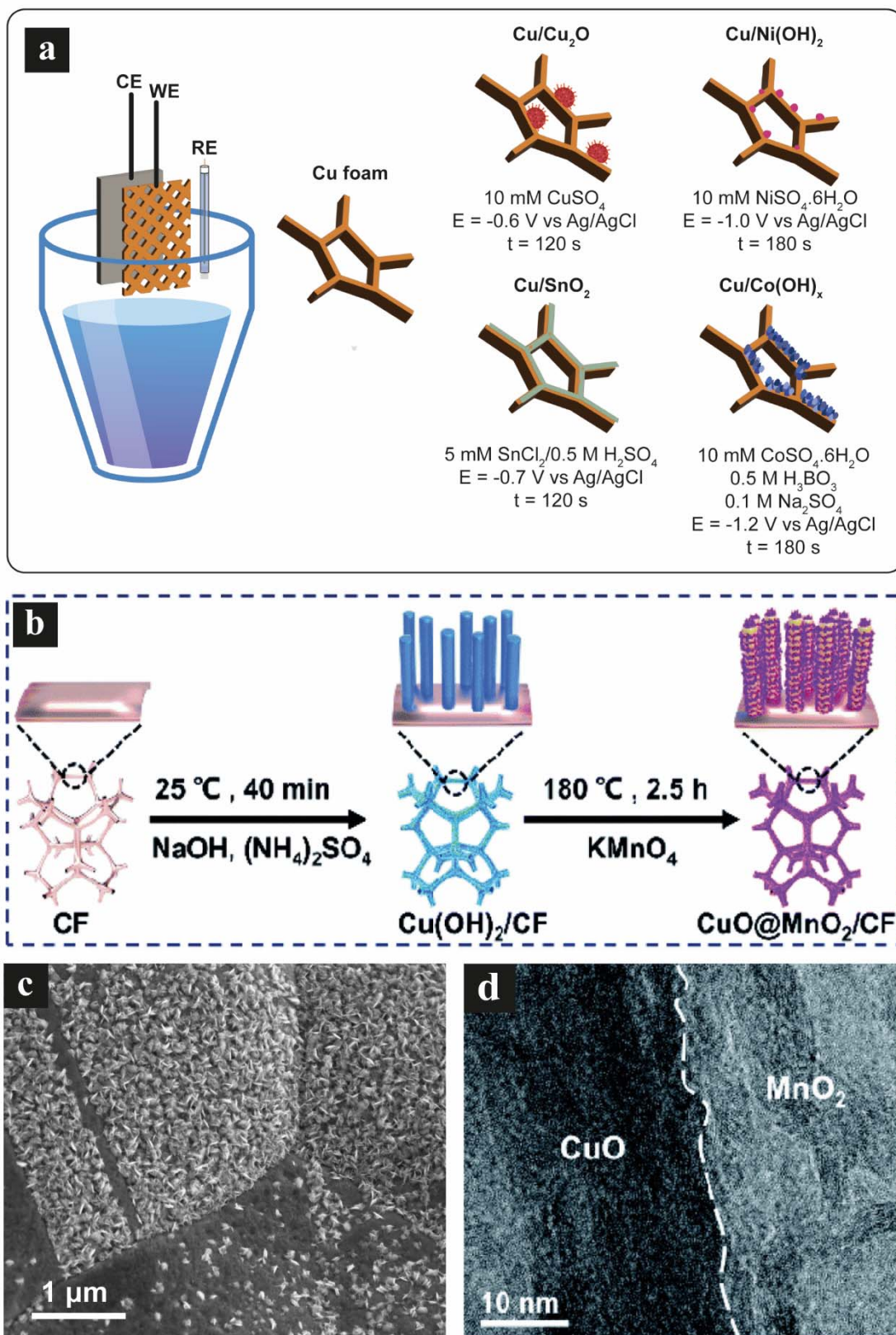
407 The modification of Cu and Ni foam electrodes has been mainly reported using two
408 techniques: electrodeposition and solvothermal method. Electrodeposition, a well-established
409 electrochemical technique, which utilizes a metal precursor in solution along with a supporting
410 electrolyte and/or additives to control deposit characteristics. Electrodeposition is typically
411 employed on flat electrode surfaces due to the homogeneity of the formed deposit. However,
412 electrodeposition on 3D metal foam electrodes results in the formation of heterogeneous deposits
413 across the thickness of the foam due to mass transfer limitations of the reactant within its 3D
414 structure. In contrast, this synthetic approach facilitates *in-situ* nucleation and growth of the
415 deposited active material, thereby providing an enhanced attachment to the foam substrate.
416 Another commonly reported technique for modifying foam electrodes is the solvothermal
417 approach, which involves crystal nucleation and growth under moderate to high temperature (100
418 – 1000 °C) and pressure (1 – 100 atm) conditions within a steel pressure vessel. In this case as
419 well, solvent, metal precursor concentration, additives, and reaction time play all a significant

420 role in the synthesis. Moreover, the synthesized material is formed and deposited on the foam
421 electrode, as well as on the solution. A direct comparison between these two electrode
422 modification techniques has shown that electrodeposited materials exhibit higher mechanical and
423 chemical stability than those deposited by solvothermal methods [88,89]. However, the total
424 loading and distribution of the synthesized material by electrodeposition through the 3D structure
425 of the foam significantly vary, reaching a more homogeneous distribution by the solvothermal
426 deposition method. This fact may directly impact the type of reactor configuration selected for
427 ERN. The flow-by configuration is well-adapted for modified foam electrodes synthesized by
428 electrodeposition because only a narrow part of the total thickness of the foam electrode
429 participates directly in the ERN, which is the one mainly containing the added material. In
430 contrast, the flow-through configuration is well-adapted for more homogenous electrodes
431 synthesized by the solvothermal deposition method because the whole thickness of the foam
432 electrode participates in the ERN.

433 Figure 4a illustrates a typical experimental setup for electrodeposition on foam electrodes,
434 featuring a three-electrodes electrochemical cell comprising a reference electrode (e.g., Ag/AgCl,
435 saturated calomel electrode (SCE)), a counter electrode (e.g., Pt plate, dimensionless stable
436 anode), and a working electrode (e.g., Ni or Cu foam). As depicted in Figure 4a, different solution
437 compositions can be employed to obtain various modified materials, with electrodeposition times
438 typically within a few minutes for nanoparticles deposition. In particular, this example illustrates
439 the modification of Cu foam by adding Cu_2O , $\text{Ni}(\text{OH})_2$, SnO_2 , or $\text{Co}(\text{OH})_x$ [90]. Figure 4b depicts
440 the hydrothermal approach for modifying Cu foam, involving a pre-treatment to oxidize the Cu
441 foam surface followed by a hydrothermal step using a solution of KMnO_4 at 180 °C for 2.5 h.
442 Compared to electrodeposition, hydrothermal procedures of synthesis involve higher temperature
443 and longer reaction times, typically in the range of a few hours for superficial modification. Figure
444 4c shows a SEM image of $\text{Cu}_{\text{foam}}/\text{Co}(\text{OH})_x$ obtained by electrodeposition, exhibiting the
445 coexistence of Cu and $\text{Co}(\text{OH})_x$ nanodomains on the electrode surface. Figure 4d presents a
446 transmission electron microscope image illustrating the solid-solid interface between MnO_2

447 particles obtained by hydrothermal treatment and previously generated CuO on the surface of Cu
448 foam.

449 In the subsequent sections, some selected studies on modified Cu and Ni foam electrodes are
450 addressed to demonstrate the lack of standardization reporting ERN performance at present and
451 some gaps in this research field are highlighted.



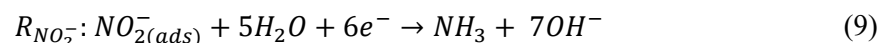
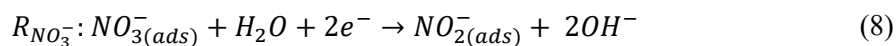
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453 **Figure 4.** (a) Sketch of experimental conditions considering electrolyte, applied potential,
 454 and time for electrodeposition of bimetallic electrodes using Cu foam as self-standing active

455 material [90]. (b) Sketch of Cu foam modification with Cu(OH)₂ and hydrothermal procedure to
 456 obtain CuO@MnO₂/CF [91]. (c) Scanning electron microscopy image of Cu/Co(OH)_x prepared
 457 by electrodeposition [90]. (d) High resolution transmission electron microscopy images of
 458 CuO@MnO₂/CF [91].

459 3.1. Modified copper foam as an active material for ERN

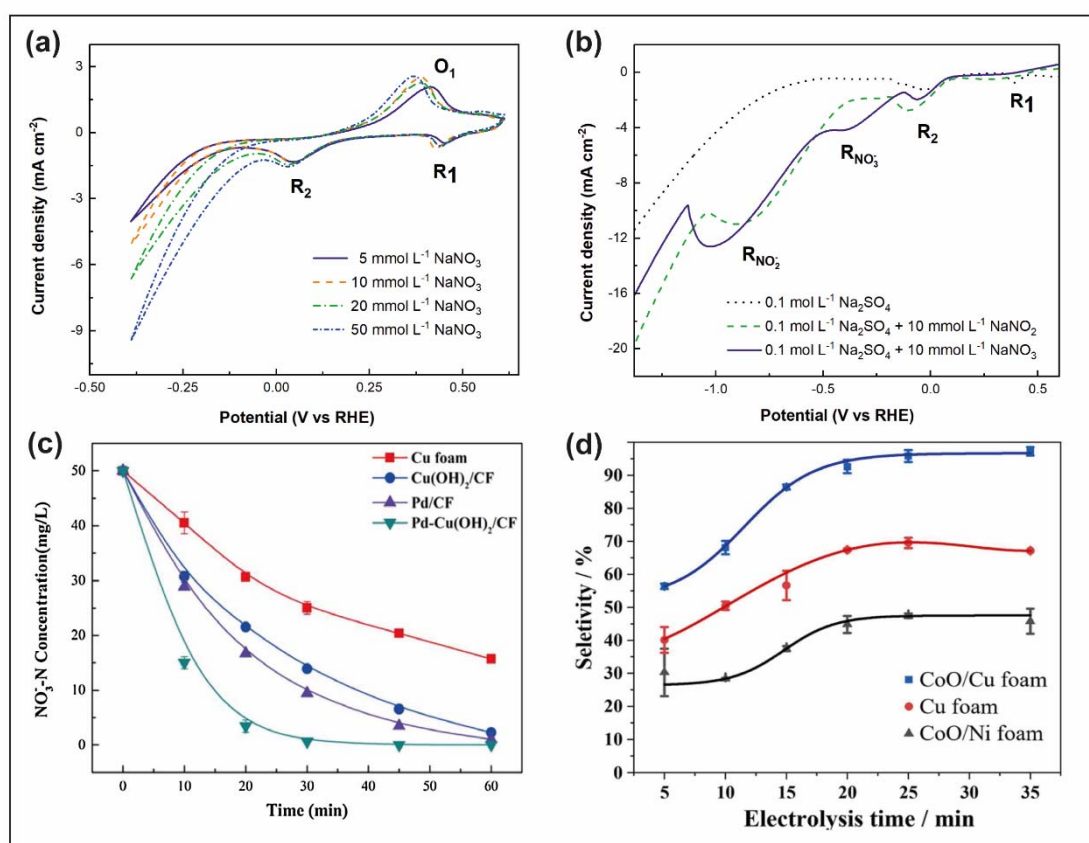
460 Copper and copper-based materials are well-recognized catalysts in ERN for facilitating the
 461 conversion of NO₃⁻ to NO₂⁻. Cu foam is a self-standing electrode material classified as type *i*)
 462 active material, which plays both roles as an active catalyst and support material. Thus, Cu foam
 463 partially contributes to the ERN electrocatalytic response in Cu_{foam}/M modified materials acting
 464 as electrocatalysts for ERN. Cerrón-Calle *et al.* reported the electrochemical behavior of bare Cu
 465 foam in the presence of a NaNO₃ solution at different concentrations to identify the characteristic
 466 reduction peaks associated with the mechanistic steps in ERN [38]. As presented in Figure 5a, the
 467 oxidation (O1) and reduction (R1 & R2) peaks associated with Cu surface modifications taking
 468 place at the electrode surface do not increase in current when the NO₃⁻ concentration in solution
 469 increases. Meanwhile, the cathodic current displayed at more negative potential than -0.15 V vs
 470 RHE increases with the concentration of NO₃⁻ in the solution. Furthermore, Figure 5b
 471 demonstrates by linear sweep voltammetry the separated contributions from NO₃⁻ reduction to
 472 NO₂⁻ (at -0.4 V vs RHE) and the further reduction of NO₂⁻ to NH₃ (at -1.0 V vs RHE), according
 473 to Equations (8) and (9), respectively.



474 The electrochemical characterization of pristine Cu foam underscores its potential to
 475 reduce NO₃⁻ to NH₃ directly in Cu foam without any additional modification. However, the main
 476 drawbacks of Cu-based materials for ERN are NO₂⁻ accumulation and low kinetic constants. To
 477 mitigate NO₂⁻ accumulation, modifying Cu foam with additional active materials to react
 478 synergistically in both reactions, Equations (8) and (9), have been extensively explored. Table 3
 479 presents some selected examples of recent studies utilizing modified Cu foam electrodes,

480 including experimental conditions and key performance parameters for activity and selectivity
481 evaluation. Additionally, Table 3 includes the ERN electrolysis results obtained by pristine Cu
482 foam electrodes under identical experimental conditions in each case. This allows to evaluate the
483 real impact of the modification incorporated into the electrode by subtracting the participation of
484 the bare Cu foam electrode. In particular, only modified Cu foam materials where several
485 consecutive cycles of electrolysis were performed to evaluate the catalyst stability are highlighted
486 in Table 3. For example, Cu_{foam}/Pt [38] and Cu_{foam}/Co(OH)_x [17] electrocatalysts are compared
487 under galvanostatic conditions with the bare Cu foam and provide a superior NO₃⁻ conversion,
488 ammonia selectivity (S_{NH3}) and faradaic efficiency (FE_{NH3}) 21-22%, as shown in Table 3.
489 Alternatively, Changhui Zhou *et al.* described the modification of Cu foam by generating
490 Cu(OH)₂ nanowires on its surface, thereby increasing the surface area available for adsorption
491 and conversion of NO₃⁻ to NO₂⁻ [92]. In addition to this, to boost the NH₃ generation, Pd sites
492 were incorporated as atomic hydrogen sources to achieve further reduction beyond NO₂⁻. Figure
493 5c illustrates the synergetic impact of these two combined modifications on the NO₃⁻ conversion
494 profile during ERN, since neither the increase in surface area produced by Cu(OH)₂ nanowires,
495 nor the presence of Pd on bare Cu foam electrodes, provide the nitrate removal efficiency reached
496 by Cu_{foam}/Cu(OH)₂/Pd electrodes. It is proposed that the incorporation of Pd sites consume the
497 NO₂⁻ produced by Cu sites, freeing up sites and accelerating the overall reaction [92]. This is
498 clearly highlighted in Table 3, where NO₃⁻ conversion by potentiostatic electrolysis reaches 100%
499 and S_{NH3} 98.8% on Cu_{foam}/Cu(OH)₂/Pd electrodes, meanwhile bare Cu foam gets blocked by the
500 rate-limiting step reaction, Equation (8), at 60% NO₃⁻ conversion and 27% S_{NH3}. Moreover, this
501 study proposes the complete removal of N from the solution by generating active chlorine species
502 during electrolysis by adding NaCl in solution and using an undivided cell. This approach
503 converts NO₃⁻ into NH₃ and then in N₂ by homogeneous reaction of NH₃ and active chlorine
504 species [15]. The approach of exploiting chemical conversion of NH₃ to N₂ has been also explored
505 by other studies shown in Table 3 [93,94]. In another recent study, Wenyang Fu *et al.* evaluated
506 the selectivity of ERN on Cu foam modified with electrodeposited CoO in a high conductivity
507 solution (0.4 M Na₂SO₄) containig 40 mM of NO₃⁻ [95]. The results of the corresponding

508 potentiostatic electrolysis are shown in Table 3 and demonstrate a net enhanced performance on
 509 Cu_{foam}/CoO electrodes with respect to bare Cu foam. The modified electrodes display 87.6% NO₃⁻
 510 conversion, 97.3% S_{NH3} and 96.7% FE_{NH3}. Moreover, the same modification based on CoO
 511 electrodeposition is applied on Cu and Ni foams to compare them. Figure 5d compares the
 512 evolution of S_{NH3} during ERN for bare Cu foam, Cu_{foam}/CoO, as well as Ni_{foam}/CoO electrodes,
 513 being clearly demonstrated in this case that the synergetic effect produced by combining CoO
 514 with Cu foam is much more relevant than the one displayed by CoO with Ni foam [95]. The
 515 Cu_{foam}/CuO@MnO₂ [91] and Cu_{foam}/Cu₃P [96] electrocatalysts have been also evaluated for ERN
 516 by potentiostatic electrolysis exhibiting in both cases an enhanced performance in comparison
 517 with Cu foam.



518

519 **Figure 5.** (a) Cyclic voltammetry at 10 mV s⁻¹ of Cu foam at different NaNO₃ concentration: 5,
 520 10, 20, and 50 mmol L⁻¹. (b) Linear sweep voltammetry at 10 mV s⁻¹ of Cu foam in presence of
 521 0.1 mol L⁻¹ Na₂SO₄ support electrolyte and with the presence of 10 mmol L⁻¹ of NaNO₃ or NaNO₂
 522 [38]. (c) NO₃⁻-N concentration evolution during ERN electrolysis on different Cu foam modified

523 materials. Experimental conditions: 50 mg L⁻¹ NO₃⁻ at -1.2 V vs Ag/AgCl for 60 min [92]. (d)
524 NH₃ selectivity evolution during ERN electrolysis on Cu and Ni foam modified electrodes.
525 Experimental conditions: 0.4 mol L⁻¹ Na₂SO₄, 0.04 mol L⁻¹ NO₃⁻ at -1.2 V vs Ag/AgCl for 35 min
526 [95].

527 **Table 3.** Some selected examples of modified Cu foam electrodes for ERN applications.

Electrode	PPI	Area (cm ²)	Experimental Conditions	NO ₃ ⁻ conversion (%)	S _{NH₃} (%)	FE _{NH₃} (%)	Stability > 90%	Ref
Cu foam	110	A _G = 2.25 *A _{ECSA} = 1.2 m ²	[Na ₂ SO ₄] = 12.5 mM [NO ₃ ⁻] = 2.1 mM j = 40 mA cm ⁻² Time = 2 h	55	55.3	11	-	[38]
Cu_{foam}/Pt	110	A _G = 2.25	Q = 648 C Undivided cell	94	84.0	22	5 cycles	
Cu foam	-	A _G = 4.0	[Na ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 2.1 mM [NaCl] = 70 mM E = -1.4 V vs Ag/AgCl Time = 2 h	2.6	-	-	5 cycles	[93]
Cu_{foam}/Cu nanobelt	-	A _G = 4.0	Undivided cell	≈100	-	-	5 cycles	
Cu foam	-	A _G = 4.0	[Na ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 3.6 mM E = -1.2 V vs Ag/AgCl Time = 5 h	61.8	20	12.9	-	[96]
Cu_{foam}/Cu₃P	-	A _G = 4.0	Q = 900 C Undivided cell	97.7	82.7	26.2	8 cycles	
Cu_{foam}/CuO	-	A _G = 2.0	[K ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 14.3 mM E = -1.3 V vs SCE Time = 2 h	91.4	84.8	83.1	-	[91]
Cu_{foam}/CuO@MnO₂	-	A _G = 2.0 *A _{ECSA} = 465.2	Divided cell	99.4	96.7	94.9	5 cycles	
Cu foam	≈100	A _G = 6.0	[Na ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 0.8 mM [NaCl] = 0.1 M E = -1.2 V vs Ag/AgCl Time = 0.75 h	60	27.0	-	-	[92]
Cu_{foam}/Cu(OH)₂/Pd	≈100	A _G = 6.0	Undivided cell	≈100	98.8	-	4 cycles	
Cu foam	-	A _G = 6.0 **A _{ECSA} = 18.6	[Na ₂ SO ₄] = 0.4 M [NO ₃ ⁻] = 40 mM E = -1.2 V vs Ag/AgCl Time = 0.58 h	33.9	67.1	72.4	-	[95]
Cu_{foam}/CoO	-	A _G = 6.0 **A _{ECSA} = 245	Undivided cell	87.6	97.3	96.7	10 cycles	
Cu foam	-	A _G = 12.0	[Na ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 7.15 mM	24.3	-	-	-	[94]

Cu_{foam}/Fe	-	A _G = 12.0	<i>j</i> = 25 mA cm ⁻² Time = 1.5 h Q = 1620 C Undivided cell	98.6	-	-	8 cycles	
Cu foam	110	A _G = 4.5 *A _{ECSA} = 1.7 m ²	[Na ₂ SO ₄] = 12.5 mM [NO ₃ ⁻] = 2.1 mM <i>j</i> = 20 mA cm ⁻² Time = 2 h Q = 648 C Undivided cells	55.3	68	11	-	
Cu_{foam}/Co(OH)_x	110	A _G = 4.5 *A _{ECSA} = 1.2 m ²		98.7	81	21	5 cycles	[17]

528 *ECSA calculated using the specific capacitance 40 μF cm⁻²

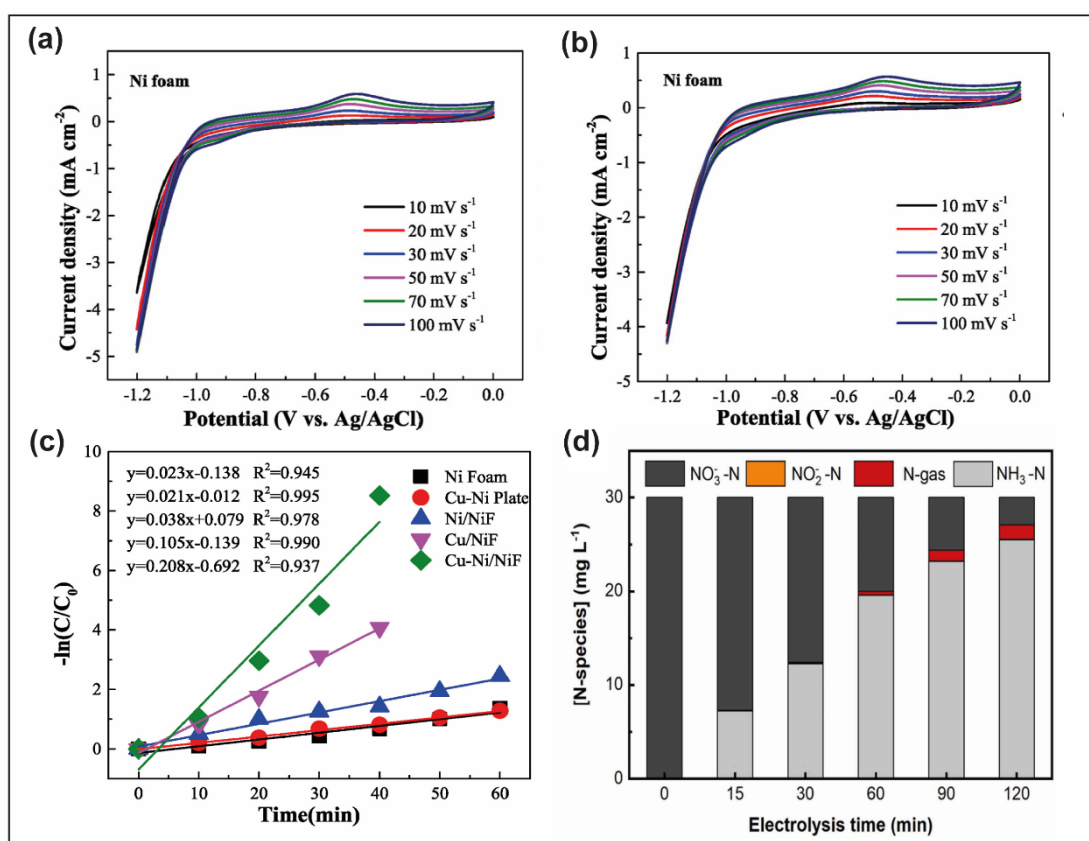
529 **ECSA calculated using the specific capacitance 60 μF cm⁻²

530

3.2. Modified nickel foam as active material for ERN

Electrodes based on Ni foam materials represent another type of metal-based 3D electrodes (type *ii*), primarily serving as support material or inactive current collector. Unlike Cu foam materials, Ni materials lack significant electrocatalytic activity for ERN. Consequently, the ERN performance of bare Ni foam electrodes is seldom reported in the literature. As studied by Xiangdong Tan *et al.*, [97], Figure 6a and Figure 6b depict the CV of bare Ni foam evaluating the electrochemical response of this material in the absence and the presence of NO_3^- , respectively. There is not a significant difference in current density when comparing both CV, which demonstrates the low electrocatalytic activity of Ni foam for ERN. Thus, the role for Ni foam is to serve as a scaffold material and facilitate the evaluation of other electrocatalytic materials on its surface [97]. Figure 6c illustrates the electrocatalytic behavior of various modified Ni foam electrodes ($\text{Ni}_{\text{foam}}/\text{M}$). In particular, $\text{Ni}_{\text{foam}}/\text{Cu}$ and $\text{Ni}_{\text{foam}}/\text{Cu-Ni}$ electrodes significantly improved kinetics for ERN. This is attributed to the intrinsic activity of these electrodeposited materials and not to the Ni foam itself [97]. This study also studies the complete removal of N from the solution by generating active chlorine species during electrolysis by adding NaCl in solution and using an undivided cell. This approach significantly improves the N_2 selectivity and has been also explored by other studies shown in Table 4. In particular, Jianan Gao *et al.*, [86] obtained 100% N_2 selectivity in the presence of $2500 \text{ mg L}^{-1} \text{ Cl}^-$ in solution. Some selected examples of recent studies utilizing modified Ni foam electrodes are presented in Table 4, including experimental conditions and key performance parameters for activity and selectivity evaluation. In particular, modified Ni foam materials where several consecutive cycles of electrolysis were performed to evaluate the catalyst stability are highlighted in Table 4. For example, a recent study by Cerron-Calle *et al.* evaluated electrodeposition of Cu and Co sites separately or combined on Ni foam as a strategy to obtain modified $\text{Ni}_{\text{foam}}/\text{M}$ electrodes exhibiting a relevant effect on ERN activity and selectivity in several cases. Figure 6d showcases the electrolysis results on $\text{Ni}_{\text{foam}}/\text{Cu}_2\text{O}/\text{Co}(\text{OH})_x$ electrode, highlighting the high NO_3^- conversion and NH_3 production achieved [39], which are almost identical to the results displayed by $\text{Cu}_{\text{foam}}/\text{Pt}$ electrode under identical experimental conditions

558 for ERN [38]. This is clearly pointed out by comparing their corresponding results reported in
 559 Tables 3 and 4. In particular, the FE_{NH_3} 22% and the NO_3^- conversion >90% are equivalent in both
 560 cases, only a slightly higher S_{NH_3} 94% on $Ni_{foam}/Cu_2O/Co(OH)_x$ electrode (Table 4) than on
 561 Cu_{foam}/Pt electrode (S_{NH_3} 84%, Table 3) is reported. Thus, it is demonstrated that type *iii*) modified
 562 electrode materials either based on Ni or Cu foam allow both to increase the ERN activity and
 563 direct its selectivity towards NH_3 production in the same magnitude. Moreover, Table 4 includes
 564 other types of Ni_{foam}/M electrocatalysts such as those based on the pyrolysis of MOF [98], as well
 565 as those based on the addition of non-metallic elements such as P ($Ni_{foam}/NiCoP$ [99]) and
 566 Ni_{foam}/CoP nanowire array [100], S ($Ni_{foam}/NiCo_2S_4$ [101]) or B ($Ni_{foam}/Ni-BO_x$ [102]). The
 567 presence of a non-metallic element in addition to metals in the ERN electrocatalyst is
 568 demonstrated to produce a significant enhancement in NO_3^- conversion, S_{NH_3} and FE_{NH_3} as is
 569 shown in Table 4.



570

571 **Figure 6.** Cyclic voltammetry of Ni foam at different scan rate in (a) absence and (b) presence of
 572 100 mg L⁻¹ NO_3^- -N in solution. (c) Pseudo-first order kinetic constants for ERN on different Ni

573 foam-based electrodes [97]. (d) NO_3^- -N conversion and products evolution during ERN
574 electrolysis using $\text{Ni}_{\text{foam}}/\text{Cu}_2\text{O}/\text{Co}(\text{OH})_x$. Experimental conditions: 30 mg L^{-1} NO_3^- -N and 12.5
575 mM Na_2SO_4 solution at 40 mA cm^{-2} for 120 min [39].

576

577 Table 4. Some selected examples of modified Ni foam electrodes for ERN applications.

Electrode	PPI	Area (cm ²)	Experimental Conditions	NO ₃ ⁻ conversion (%)	S _{NH3} (%)	FE _{NH3} (%)	Stability > 90%	Ref
Ni _{foam} /P-doped-Co ₃ O ₄	-	A _G =8 **A _{ECSA} = 1008	[Na ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 3.6 mM E = -1.3 V vs SCE Time = 2 h Undivided cell	98	78	31.4	10 cycles	[86]
Ni foam	110	A _G = 2.25 *A _{ECSA} = 1913	[Na ₂ SO ₄] = 12.5 mM [NO ₃ ⁻] = 2.1 mM j = 40 mA cm ⁻² Time = 2 h Q = 648 C Undivided cell	9.6	95.8	2	-	[39]
Ni _{foam} /Cu ₂ O	110	A _G = 2.0 *A _{ECSA} = 4838		28.4	49.5	4	-	
Ni _{foam} /Co(OH) _x	110	A _G = 2.0 *A _{ECSA} = 2813		86.7	87.5	20	6 cycles	
Ni _{foam} /Cu ₂ O/Co(OH) _x	110	A _G = 2.0 *A _{ECSA} = 3518		90.3	94	22	6 cycles	
Ni _{foam} /MnO ₂ -Oxygen vacancy	110	A _G =8	[Na ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 1.6 mM E = -0.85 V vs Ag/AgCl Time = 6 h Divided continuous-flow cell	15.9	34.5	62.2	-	[103]
Ni _{foam} /Pd	110	A _G =8		53.3	85	69.7	-	
Ni _{foam} /MnO ₂ -Oxygen vacancy-Pd	110	A _G =8		90.6	87.6	69.6	-	
Ni _{foam} /Fe@Fe ₂ O ₃	-	*A _{ECSA} = 6.5	[Na ₂ SO ₄] = 0.1 M [NO ₃ ⁻] = 3.6 mM E = -1.35 V vs Ag/AgCl	86.1	93	-	-	[98]

Ni_{foam}/Co-Fe@Fe₂O₃	-	*A _{ECSA} = 37.75	Time = 10 h Undivided cell	96.7	99	85.2	8 cycles	
Ni_{foam}/NiCo	-	A _G = 5	[Na ₂ SO ₄] = 50 mM [NO ₃ ⁻] = 3.6 mM j = 2 mA cm ⁻² Time = 5 h	82	73.4	43.5	-	[99]
Ni_{foam}/NiCoP	-	A _G = 5	Q = 180 C Divided cell	97.7	95.4	57.7	6 cycles	
Ni_{foam}/Co(OH)₂ nanowire array	-	A _G = 1.5 *A _{ECSA} = 17	[Na ₂ SO ₄] = 0.2 M [NO ₃ ⁻] = 7.14 mM	7.8	86.9	-	-	
Ni_{foam}/Co₃O₄ nanowire array	-	A _G = 1.5 *A _{ECSA} = 5	E = -0.7 V vs RHE Time = 3 h Undivided cell	13.9	88.1	-	-	[100]
Ni_{foam}/CoP nanowire array	-	A _G = 1.5 *A _{ECSA} = 857		97.9	99.4	97	10 cycles	
Ni_{foam}/NiCo₂O₄	-	A _G = 2 A _{ECSA} = 592.5	[KOH] = 1.0 M [NO ₃ ⁻] = 3.6 mM E = -1.4 V vs Ag/AgCl Time = 2 h	60.5	76.9			[101]
Ni_{foam}/NiCo₂S₄	-	A _G = 2 A _{ECSA} = 1006.25	Divided cell	89.6	92.1	45.4	8 cycles	
Ni foam	-	A _G = 0.09 *A _{ECSA} = 1.0	[Na ₂ SO ₄] = 0.1 M [NO ₃ ⁻] = 500 mM E = -0.9 V vs RHE Time = 0.5 h	-		49	-	[102]
Ni_{foam}/Ni-BO_x	-	A _G = 0.09 *A _{ECSA} = 1.7	Undivided cell	-		94	30 cycles	

578 *ECSA calculated using the specific capacitance 40 μF cm⁻²

579 **ECSA calculated using the specific capacitance 60 μF cm⁻²

580

581 The literature on metal-3D foam electrodes for ERN is extensive, but comparing different
582 electrode materials remains challenging due to the lack of normalization of experimental
583 conditions, reported parameters, and operation methods. Nevertheless, comparing the selected
584 results shown in Tables 3 and 4 allows us to identify five keypoints to be improved in the future.

585 (1) The *PPI* metric is only reported in 30 % of the studies considered. This suggests that
586 either only one value is commonly reported for this parameter or its importance is often
587 overlooked. However, it is crucial to note that various *PPI* values ranging from 5 to 130 are
588 available in the commercially available foams. As previously discussed, *PPI* plays a pivotal role
589 in mass transfer at the electrode surface, making it crucial for controlling the interfacial pH.
590 Therefore, by considering *PPI* as a fixed parameter, the benchmarking process is limited to a very
591 few number of studies.

592 (2) The electrode area, whether geometrical or ECSA, is essential for a comprehensive
593 comparison among the array of electrocatalysts prepared. However, according to the studies
594 considered, geometric 2D area ($W \times L$) is commonly used for reporting performance, overlooking
595 the true effects of 3D structures. Consequently, parameters such as areal density ($\text{cm}^2 \text{g}^{-1}$) or
596 specific surface area (SSA, $\text{cm}^2 \text{cm}^{-3}$) are often neglected. Similarly, ECSA, crucial for intrastudy
597 benchmarking of electrocatalysts and providing insight into modified material and their intrinsic
598 activity (as suggested in Figure 1), is not consistently reported. A more meticulous
599 electrochemical interstudy benchmarking of electrocatalysts requires the estimation of ECSA for
600 a better understanding of the electrochemical system, which is urgently needed. Therefore,
601 reporting both geometric area and ECSA should be promoted as a good practice to enhance the
602 benchmarking of electrocatalysts both within and across studies.

603 (3) Variations in experimental conditions such as initial NO_3^- concentration and
604 electrolyte composition make it difficult to compare different studies, despite most studies
605 providing NO_3^- conversion and NH_3 selectivity evaluation. For instance, Cu foam (Table 3, [95])
606 exhibits a NO_3^- conversion of 33.9 % and a NH_3 selectivity of 67.1 %, while $\text{Ni}_{\text{foam}}/\text{Pd}$ (Table 4,
607 [103]) shows 53.3 % and 85%, respectively. Based solely on conversion values, $\text{Ni}_{\text{foam}}/\text{Pd}$ appears

608 to exhibit higher activity, potentially leading to an increased NH_3 production. However, such
609 comparisons are inaccurate without considering the initial NO_3^- concentration. Using the reported
610 initial conditions (40 mM NO_3^- for Cu foam and 1.6 mM NO_3^- for $\text{Ni}_{\text{foam}}/\text{Pd}$), Cu foam generates
611 approximately 127 mg $\text{NH}_3\text{-N L}^{-1}$ and $\text{Ni}_{\text{foam}}/\text{Pd}$ 10.14 mg $\text{NH}_3\text{-N L}^{-1}$. This highlights the
612 challenge of benchmarking electrodes using these parameters, which involves considering the
613 initial NO_3^- concentration and subsequent calculations to enable direct comparison. Furthermore,
614 the absence of standardized conditions results in a chaotic range of conditions, with initial NO_3^-
615 concentrations varying from 1 to 40 mM for Cu-based electrodes (Table 3) and from 2 to 500 mM
616 for Ni-based electrodes (Table 4).

617 (4) Similarly to the wide range of initial NO_3^- concentrations, electrochemical conditions
618 are not standardized across studies. Under potentiostatic conditions, reported potentials in
619 electrolysis correspond to those determined during the evaluation of intrinsic activity. However,
620 key parameters such as supporting electrolytes, initial pH, and electrolysis time are often different.
621 A subset of studies performs electrolysis under galvanostatic conditions, employing current
622 densities ranging from 2 to 40 mA cm^{-2} , but without considering a benchmark and constant
623 number of coulombs circulated during the electrolysis to facilitate subsequent results comparison.
624 Notably, comparing results from Tables 3 and 4 reveals some trends; for example, disparities in
625 FE_{NH_3} arise when comparing constant potential electrolysis (mostly $\text{FE}_{\text{NH}_3} \geq 70\%$) with constant
626 current electrolysis (mostly $\text{FE}_{\text{NH}_3} < 30\%$). The main reason for these disparities lies in the
627 competitive hydrogen evolution reaction (HER), which occurs at a similar potential to ERN. HER
628 can be modulated by controlling the applied potential, whereas this control is absent in constant
629 current electrolysis. Consequently, the quantification of H_2 gas produced during ERN electrolysis
630 represents a significant gap in most ERN studies, which is typically overlooked. Comparison
631 across operation methods is incorrect as it will not illustrate the competitiveness of
632 electrocatalysts under identical conditions. Furthermore, the reader should note that real upscale
633 applications generally operate under galvanostatic conditions in large electrochemically

634 engineered systems beyond the lab bench (which would correspond to the studies that report the
635 lower FE_{NH_3} values in literature).

636 (5) The most commonly used benchmarking parameter for ERN in the literature, NH_3
637 yield ($mmol NH_3 g^{-1}_{cat} h^{-1}$ or $mmol NH_3 cm^{-2}_{cat} h^{-1}$), directly incorporates NH_3 production
638 normalized by catalyst mass or area, and time. However, the disparities between geometrical and
639 ECSA areas introduce additional errors in reporting NH_3 yield. This parameter introduces another
640 source of confusion since at high initial NO_3^- concentrations, NH_3 yield produced on a poor
641 electrocatalyst may appear higher than that obtained using an optimal electrode, but treating a
642 lower initial NO_3^- concentration. Therefore, there is an urgent need to incorporate additional
643 parameters, which consider the initial NO_3^- concentration to avoid misunderstandings and
644 facilitate benchmarking, as well as evaluate the overpotential and, thus, the energy required to
645 produce NH_3 . We have recently proposed NH_3 generation efficiency (Equation (10)) [90], which
646 combines both concepts, selectivity and conversion.

$$647 \quad NH_3 \text{ generation efficiency (\%)} = \frac{C_{NH_3,exp}}{C_{NH_3,theo}} \times 100 \quad (10)$$

648 where $C_{NH_3,exp}$ is the NH_3 concentration experimentally obtained from electrolysis in
649 $mmol L^{-1}$ and $C_{NH_3,theo}$ is the theoretical NH_3 concentration in $mmol L^{-1}$ if the entire initial amount
650 of NO_3^- is converted to NH_3 by ERN.

651 Concerning the overpotential evaluation in NO_3^- conversion, we propose to adapt the
652 parameter of energy efficiency (Equation (11)), which is commonly used to evaluate
653 electrochemical CO_2 reduction performance [104,105].

$$654 \quad NH_3 \text{ energy efficiency (\%)} = (E_T/E) \times FE_{NH_3} \quad (11)$$

655 where E_T is the thermodynamic potential in volts required for the electrocatalytic
656 reduction of NO_3^- to NH_3 in aqueous solution, whereas E and FE_{NH_3} represent the experimental
657 cathode potential applied in volts and the NH_3 Faradaic Efficiency (%), respectively.

658

659 4. Conclusions and outlook

660 The ERN systems have emerged as a promising approach for resource recovery, particularly
661 in NH_3 production. Rational electrode design has guided researchers through various
662 configurations, with metal-based 3D electrodes showing considerable potential in material design.
663 Specifically, self-standing Cu and Ni foam electrodes have been extensively studied for their roles
664 as electrocatalytic active and support materials, respectively. This review addresses two critical
665 parameters characterizing foam electrodes often overlooked in ERN literature: pore per inch (*PPI*)
666 and electrochemically active surface area (ECSA), as well as proposes two additional engineering
667 figures of merit for benchmarking ERN by encompassing selectivity and conversion and
668 evaluating overpotential contribution.

669 The importance of *PPI* is revalued, emphasizing its significant role in reactants and products
670 mass transfer, and suggesting its crucial relevance in evaluating water matrices to prevent
671 inorganic and organic scaling. However, the lack of studies using full reactors (flow-through or
672 flow-by) conceals the benefits of 3D metal foam for ERN. Additionally, the indirect measurement
673 of ECSA is promoted, with main steps provided for reliable calculations. Techniques such as
674 cyclic voltammetry or electrochemical impedance spectroscopy can be utilized to estimate ECSA,
675 with consistency across studies recommended for proper evaluation of modified Cu and Ni foam
676 electrodes ($\text{Cu}_{\text{foam}}/\text{M}$ and $\text{Ni}_{\text{foam}}/\text{M}$).

677 At present, benchmarking electrocatalysts for ERN presents more challenges than certainties.
678 Despite ERN's potential as a resource recovery approach, the lack of specific trends and variety
679 among studies creates a complex scenario where comparability is limited. Significant advances
680 have been made in electrocatalyst design, but some reference values have not been identified yet.
681 The current lack of standardization in reporting *PPI*, ECSA, experimental conditions, and key
682 performance metrics hinders meaningful comparisons across ERN studies. This variability limits
683 a broader understanding of the ERN and obscures the identification of optimal electrode materials
684 and operating parameters. Reviewing $\text{Cu}_{\text{foam}}/\text{M}$ and $\text{Ni}_{\text{foam}}/\text{M}$ studies reveals nuances based on
685 various aspects, prompting reconsideration of the composition of the solution to be treated and

686 the need to set reference concentrations for both reactant and supporting electrolyte, as well as
687 using a constant amount of circulated charge to compare different electrolysis properly.
688 Morphological and structural analysis of the electrode before and after ERN electrolysis is notably
689 absent in the literature. Similarly, accelerated life tests for these 3D foam electrodes are rarely
690 considered.

691 From this perspective, several key research directions are essential and require future
692 development. Reactor configurations designed to optimize 3D foam electrodes and strategies to
693 suppress the competitive HER could significantly improve ERN efficiency. Exploring
694 electrocatalytic materials that selectively inhibit HER without impacting ERN could be a
695 promising research direction, particularly relevant in galvanostatic electrolysis. Additionally,
696 investigations in electrode stability under realistic water conditions by accelerated tests,
697 considering potential issues like inorganic scaling, are crucial for practical applications.

698 The benchmarking of 3D electrodes for ERN represents a significant challenge, as highlighted
699 by the nuances and gaps identified in this review. It is evident that the current state of research
700 lacks characterization protocols and standardized reporting practices, which hinders effective
701 comparison of electrode performance across studies. By addressing these challenges, we should
702 be able to accelerate the development of highly efficient, selective, and scalable ERN systems,
703 propelling this technology, still under development, from a low technology readiness level (TRL)
704 towards a widespread water treatment technology. While significant advances have been made in
705 understanding the fundamental principles of ERN and exploring novel electrodes configurations,
706 there remains a need for practical implementation and field testing under real-world conditions.

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718

719 **5. References**

- 720 [1] A.J. dos Santos, H.L. Barazorda-Ccahuana, G. Caballero-Manrique, Y. Chérémond, P.J.
721 Espinoza-Montero, J.R. González-Rodríguez, U.J. Jáuregui-Haza, M.R.V. Lanza, A.
722 Nájera, C. Oporto, A. Pérez Parada, T. Pérez, V.D. Quezada, V. Rojas, V. Sosa, A.
723 Thiam, R.A. Torres-Palma, R. Vargas, S. Garcia-Segura, Accelerating innovative water
724 treatment in Latin America, *Nat. Sustain.* (2023). [https://doi.org/10.1038/s41893-022-](https://doi.org/10.1038/s41893-022-01042-z)
725 01042-z.
- 726 [2] I. Jeon, E.C. Ryberg, P.J.J. Alvarez, J.H. Kim, Technology assessment of solar
727 disinfection for drinking water treatment, *Nat. Sustain.* 5 (2022).
728 <https://doi.org/10.1038/s41893-022-00915-7>.
- 729 [3] N. Singh, B.R. Goldsmith, Role of Electrocatalysis in the Remediation of Water
730 Pollutants, *ACS Catal.* 10 (2020) 3365–3371. <https://doi.org/10.1021/acscatal.9b04167>.
- 731 [4] I. Katsounaros, On the assessment of electrocatalysts for nitrate reduction, *Curr. Opin.*
732 *Electrochem.* 28 (2021) 100721. <https://doi.org/10.1016/j.coelec.2021.100721>.
- 733 [5] D. Cecconet, F. Sabba, M. Devecseri, A. Callegari, A.G. Capodaglio, In situ
734 groundwater remediation with bioelectrochemical systems: A critical review and future
735 perspectives, *Environ. Int.* 137 (2020) 105550.
736 <https://doi.org/10.1016/j.envint.2020.105550>.
- 737 [6] M.J. Pennino, J.E. Compton, S.G. Leibowitz, Trends in Drinking Water Nitrate
738 Violations Across the United States, *Environ. Sci. Technol.* 51 (2017) 13450–13460.
739 <https://doi.org/10.1021/acs.est.7b04269>.
- 740 [7] M. Allaire, H. Wu, U. Lall, National trends in drinking water quality violations, *Proc.*
741 *Natl. Acad. Sci. U. S. A.* 115 (2018) 2078–2083.
742 <https://doi.org/10.1073/pnas.1719805115>.
- 743 [8] M. Allaire, H. Wu, U. Lall, National trends in drinking water quality violations, *Proc.*

- 744 Natl. Acad. Sci. U. S. A. 115 (2018) 2078–2083.
745 <https://doi.org/10.1073/pnas.1719805115>.
- 746 [9] R. Epsztein, O. Nir, O. Lahav, M. Green, Selective nitrate removal from groundwater
747 using a hybrid nanofiltration-reverse osmosis filtration scheme, *Chem. Eng. J.* 279
748 (2015) 372–378. <https://doi.org/10.1016/j.cej.2015.05.010>.
- 749 [10] A.M. Bergquist, J.K. Choe, T.J. Strathmann, C.J. Werth, Evaluation of a hybrid ion
750 exchange-catalyst treatment technology for nitrate removal from drinking water, *Water*
751 *Res.* 96 (2016) 177–187. <https://doi.org/10.1016/j.watres.2016.03.054>.
- 752 [11] S. Singh, A.G. Anil, V. Kumar, D. Kapoor, S. Subramanian, J. Singh, P.C. Ramamurthy,
753 Nitrates in the environment: A critical review of their distribution, sensing techniques,
754 ecological effects and remediation, *Chemosphere.* 287 (2022) 131996.
755 <https://doi.org/10.1016/j.chemosphere.2021.131996>.
- 756 [12] B.K. Pramanik, L. Shu, V. Jegatheesan, A review of the management and treatment of
757 brine solutions, *Environ. Sci. Water Res. Technol.* 3 (2017) 625–658.
758 <https://doi.org/10.1039/c6ew00339g>.
- 759 [13] J. Sanchis-Carbonell, I. Carrero-Ferrer, A. Sáez-Fernández, M. Pedro-Monzonis, P.
760 Campíns-Falcó, V. Montiel, Towards a zero liquid discharge process from brine
761 treatment: Water recovery, nitrate electrochemical elimination and potential valorization
762 of hydrogen and salts, *Sci. Total Environ.* 926 (2024).
763 <https://doi.org/10.1016/j.scitotenv.2024.172060>.
- 764 [14] S. Garcia-Segura, M. Lanzarini-Lopes, K. Hristovski, P. Westerhoff, Electrocatalytic
765 reduction of nitrate: Fundamentals to full-scale water treatment applications, *Appl. Catal.*
766 *B Environ.* 236 (2018) 546–568. <https://doi.org/10.1016/j.apcatb.2018.05.041>.
- 767 [15] K. Flores, G.A. Cerrón-Calle, C. Valdes, A. Atrashkevich, A. Castillo, H. Morales, J.G.
768 Parsons, S. Garcia-Segura, J.L. Gardea-Torresdey, Outlining Key Perspectives for the

769 Advancement of Electrocatalytic Remediation of Nitrate from Polluted Waters, ACS
770 ES&T Eng. 2 (2022) 746–768. <https://doi.org/10.1021/acsestengg.2c00052>.

771 [16] M. Marcos-Hernández, G. Antonio Cerrón-Calle, Y. Ge, S. Garcia-Segura, C.M.
772 Sánchez-Sánchez, A.S. Fajardo, D. Villagrán, Effect of surface functionalization of
773 Fe₃O₄ nano-enabled electrodes on the electrochemical reduction of nitrate, Sep. Purif.
774 Technol. 282 (2022) 119771. <https://doi.org/10.1016/j.seppur.2021.119771>.

775 [17] G.A. Cerrón-Calle, A.S. Fajardo, J. Liu, C.M. Sánchez-Sánchez, S. Garcia-Segura,
776 Enabling circular economy by N-recovery: Electrocatalytic reduction of nitrate with
777 cobalt hydroxide nanocomposites on copper foam treating low conductivity groundwater
778 effluents, Sci. Total Environ. 887 (2023) 163938.
779 <https://doi.org/10.1016/j.scitotenv.2023.163938>.

780 [18] D. Anastasiadou, Y. van Beek, W. Chen, T. Wissink, A. Parastaev, E.J.M. Hensen, M.
781 Costa Figueiredo, Morphology Changes of Cu₂O Catalysts During Nitrate
782 Electroreduction to Ammonia**, ChemCatChem. 15 (2023) 1–9.
783 <https://doi.org/10.1002/cctc.202201503>.

784 [19] A.S. Fajardo, P. Westerhoff, S. Garcia-Segura, C.M. Sánchez-Sánchez, Selectivity
785 modulation during electrochemical reduction of nitrate by electrolyte engineering, Sep.
786 Purif. Technol. 321 (2023) 124233. <https://doi.org/10.1016/j.seppur.2023.124233>.

787 [20] J.M. McEnaney, S.J. Blair, A.C. Nielander, J.A. Schwalbe, D.M. Koshy, M. Cargnello,
788 T.F. Jaramillo, Electrolyte engineering for efficient electrochemical nitrate reduction to
789 ammonia on a titanium electrode, ACS Sustain. Chem. Eng. 8 (2020) 2672–2681.
790 <https://doi.org/10.1021/acssuschemeng.9b05983>.

791 [21] I. Sanjuán, L. García-Cruz, J. Solla-Gullón, E. Expósito, V. Montiel, Bi–Sn
792 nanoparticles for electrochemical denitrification: activity and selectivity towards N₂
793 formation, Electrochim. Acta. 340 (2020).
794 <https://doi.org/10.1016/j.electacta.2020.135914>.

- 795 [22] D.R. MacFarlane, P. V. Cherepanov, J. Choi, B.H.R. Suryanto, R.Y. Hodgetts, J.M.
796 Bakker, F.M. Ferrero Vallana, A.N. Simonov, A Roadmap to the Ammonia Economy,
797 *Joule*. 4 (2020) 1186–1205. <https://doi.org/10.1016/j.joule.2020.04.004>.
- 798 [23] P.H. van Langevelde, I. Katsounaros, M.T.M. Koper, Electrocatalytic Nitrate Reduction
799 for Sustainable Ammonia Production, *Joule*. 5 (2021) 290–294.
800 <https://doi.org/10.1016/j.joule.2020.12.025>.
- 801 [24] H. Yin, X. Xing, W. Zhang, J. Li, W. Xiong, H. Li, A simple hydrothermal synthesis of
802 an oxygen vacancy-rich MnMoO₄ rod-like material and its highly efficient
803 electrocatalytic nitrogen reduction, *Dalt. Trans.* 52 (2023) 16670–16679.
804 <https://doi.org/10.1039/d3dt03018k>.
- 805 [25] X. Huang, X. Xing, W. Xiong, H. Li, Flower-Like Ni-Mn Bimetallic Oxide-Based
806 Nanosheets for Enhanced Electrocatalytic Nitrogen Reduction to Ammonia, *Energy and*
807 *Fuels*. 37 (2023) 19147–19155. <https://doi.org/10.1021/acs.energyfuels.3c03517>.
- 808 [26] G.A. Cerrón-Calle, T.P. Senftle, S. Garcia-Segura, Strategic tailored design of
809 electrocatalysts for environmental remediation based on density functional theory (DFT)
810 and microkinetic modeling, *Curr. Opin. Electrochem.* 35 (2022) 101062.
811 <https://doi.org/10.1016/j.coelec.2022.101062>.
- 812 [27] Y. Wang, W. Zhou, R. Jia, Y. Yu, B. Zhang, Unveiling the Activity Origin of a Copper-
813 based Electrocatalyst for Selective Nitrate Reduction to Ammonia, *Angew. Chemie - Int.*
814 *Ed.* 59 (2020) 5350–5354. <https://doi.org/10.1002/anie.201915992>.
- 815 [28] D. Hao, Z. gang Chen, M. Figiela, I. Stepniak, W. Wei, B.J. Ni, Emerging alternative for
816 artificial ammonia synthesis through catalytic nitrate reduction, *J. Mater. Sci. Technol.*
817 77 (2021) 163–168. <https://doi.org/10.1016/j.jmst.2020.10.056>.
- 818 [29] L. Yang, J. Li, F. Du, J. Gao, H. Liu, S. Huang, H. Zhang, C. Li, C. Guo, Interface
819 engineering cerium-doped copper nanocrystal for efficient electrochemical nitrate-to-

- 820 ammonia production, *Electrochim. Acta.* 411 (2022) 140095.
821 <https://doi.org/10.1016/j.electacta.2022.140095>.
- 822 [30] Z. Niu, S. Fan, X. Li, J. Duan, A. Chen, Interfacial engineering of CoMn₂O₄/NC
823 induced electronic delocalization boosts electrocatalytic nitrogen oxyanions reduction to
824 ammonia, *Appl. Catal. B Environ.* 322 (2023) 122090.
825 <https://doi.org/10.1016/j.apcatb.2022.122090>.
- 826 [31] A. Atrashkevich, A.S. Fajardo, P. Westerhoff, W.S. Walker, C.M. Sánchez-Sánchez, S.
827 Garcia-Segura, Overcoming barriers for nitrate electrochemical reduction: By-passing
828 water hardness, *Water Res.* 225 (2022) 119118.
829 <https://doi.org/10.1016/j.watres.2022.119118>.
- 830 [32] J. Ma, W. Wei, G. Qin, T. Xiao, W. Tang, S. Zhao, L. Jiang, S. Liu, Electrochemical
831 reduction of nitrate in a catalytic carbon membrane nano-reactor, *Water Res.* 208 (2022)
832 117862. <https://doi.org/10.1016/j.watres.2021.117862>.
- 833 [33] J. Li, G. Zhan, J. Yang, F. Quan, C. Mao, Y. Liu, B. Wang, F. Lei, L. Li, A.W.M. Chan,
834 L. Xu, Y. Shi, Y. Du, W. Hao, P.K. Wong, J. Wang, S.X. Dou, L. Zhang, J.C. Yu,
835 Efficient Ammonia Electrosynthesis from Nitrate on Strained Ruthenium Nanoclusters,
836 *J. Am. Chem. Soc.* 142 (2020) 7036–7046. <https://doi.org/10.1021/jacs.0c00418>.
- 837 [34] A. Iarchuk, A. Dutta, P. Broekmann, Novel Ni foam catalysts for sustainable nitrate to
838 ammonia electroreduction, *J. Hazard. Mater.* 439 (2022) 129504.
839 <https://doi.org/10.1016/j.jhazmat.2022.129504>.
- 840 [35] A. Kulshreshtha, S.K. Dhakad, Preparation of metal foam by different methods: A
841 review, *Mater. Today Proc.* 26 (2019) 1784–1790.
842 <https://doi.org/10.1016/j.matpr.2020.02.375>.
- 843 [36] M. Grdeń, M. Alsabet, G. Jerkiewicz, Surface science and electrochemical analysis of
844 nickel foams, *ACS Appl. Mater. Interfaces.* 4 (2012) 3012–3021.

- 845 <https://doi.org/10.1021/am300380m>.
- 846 [37] A.S. Fajardo, P. Westerhoff, C.M. Sanchez-Sanchez, S. Garcia-Segura, Earth-abundant
847 elements a sustainable solution for electrocatalytic reduction of nitrate, *Appl. Catal. B*
848 *Environ.* 281 (2021) 119465. <https://doi.org/10.1016/j.apcatb.2020.119465>.
- 849 [38] G.A. Cerrón-Calle, A.S. Fajardo, C.M. Sánchez-Sánchez, S. Garcia-Segura, Highly
850 reactive Cu-Pt bimetallic 3D-electrocatalyst for selective nitrate reduction to ammonia,
851 *Appl. Catal. B Environ.* 302 (2022) 120844.
852 <https://doi.org/10.1016/j.apcatb.2021.120844>.
- 853 [39] G.A. Cerrón-Calle, A. Wines, S. Garcia-Segura, Atomic hydrogen provision by cobalt
854 sites in a bimetallic Ni/Co(OH)_x and trimetallic Ni/Cu₂O/Co(OH)_x configurations for
855 superior ammonia production, *Appl. Catal. B Environ.* 328 (2023) 122540.
856 <https://doi.org/10.1016/j.apcatb.2023.122540>.
- 857 [40] C.C.L. McCrory, S. Jung, J.C. Peters, T.F. Jaramillo, Benchmarking heterogeneous
858 electrocatalysts for the oxygen evolution reaction, *J. Am. Chem. Soc.* 135 (2013) 16977–
859 16987. <https://doi.org/10.1021/ja407115p>.
- 860 [41] Y. Guan, W. Suo, Z. Zhang, Y. Wang, S. Sun, G. Liu, Insights on the Catalytic Active
861 Site for CO₂ Reduction on Copper-based Catalyst: A DFT study, *Mol. Catal.* 511 (2021)
862 111725. <https://doi.org/10.1016/j.mcat.2021.111725>.
- 863 [42] N. Atrak, E. Tayyebi, E. Skúlason, Effect of co-adsorbed water on electrochemical CO₂
864 reduction reaction on transition metal oxide catalysts, *Appl. Surf. Sci.* 570 (2021)
865 151031. <https://doi.org/10.1016/j.apsusc.2021.151031>.
- 866 [43] D. Jang, J. Maeng, J. Kim, H. Han, G.H. Park, J. Ha, D. Shin, Y.J. Hwang, W.B. Kim,
867 Boosting electrocatalytic nitrate reduction reaction for ammonia synthesis by plasma-
868 induced oxygen vacancies over MnCuO_x, *Appl. Surf. Sci.* 610 (2023) 155521.
869 <https://doi.org/10.1016/j.apsusc.2022.155521>.

- 870 [44] W. Zheng, Y. Chen, X. Peng, K. Zhong, Y. Lin, Z. Huang, The phase evolution and
871 physical properties of binary copper oxide thin films prepared by reactive magnetron
872 sputtering, *Materials (Basel)*. 10 (2018) 1–13. <https://doi.org/10.3390/ma11071253>.
- 873 [45] M.I. Pintor-Monroy, D. Barrera, B.L. Murillo-Borjas, F.J. Ochoa-Estrella, J.W.P. Hsu,
874 M.A. Quevedo-Lopez, Tunable Electrical and Optical Properties of Nickel Oxide (NiO x
875) Thin Films for Fully Transparent NiO x -Ga 2 O 3 p-n Junction Diodes, *ACS Appl.*
876 *Mater. Interfaces*. 10 (2018) 38159–38165. <https://doi.org/10.1021/acsami.8b08095>.
- 877 [46] N.D. Koshel', V. V. Malyshev, Measurement of the resistivity of the electrode
878 NiOOH/Ni(OH)₂ solid phase active substance during the discharge process, *Surf. Eng.*
879 *Appl. Electrochem.* 46 (2010) 348–351. <https://doi.org/10.3103/S1068375510040095>.
- 880 [47] H. Bartzsch, D. Glöß, B. Böcher, P. Frach, K. Goedicke, Properties of SiO₂ and Al₂O₃
881 films for electrical insulation applications deposited by reactive pulse magnetron
882 sputtering, *Surf. Coatings Technol.* 174–175 (2003) 774–778.
883 [https://doi.org/10.1016/S0257-8972\(03\)00384-0](https://doi.org/10.1016/S0257-8972(03)00384-0).
- 884 [48] J. Liu, J. Dang, M. Wang, X. Wang, X. Duan, S. Yuan, T. Liu, Q. Wang, Metal–
885 Organic-Framework-Derived Cobalt nanoparticles encapsulated in Nitrogen-Doped
886 carbon nanotubes on Ni foam integrated Electrode: Highly electroactive and durable
887 catalysts for overall water splitting, *J. Colloid Interface Sci.* 606 (2022) 38–46.
888 <https://doi.org/10.1016/j.jcis.2021.07.152>.
- 889 [49] W. Wu, J. Liu, N. Johannes, Electrodeposition of Ir–Co thin films on copper foam as
890 high-performance electrocatalysts for efficient water splitting in alkaline medium, *Int. J.*
891 *Hydrogen Energy*. 46 (2021) 609–621. <https://doi.org/10.1016/j.ijhydene.2020.09.268>.
- 892 [50] N. Girichandran, S. Saedy, R. Kortlever, Electrochemical CO₂ reduction on a copper
893 foam electrode at elevated pressures, *Chem. Eng. J.* 487 (2024) 150478.
894 <https://doi.org/10.1016/j.cej.2024.150478>.

- 895 [51] W. Zheng, M. Liu, L.Y.S. Lee, Best Practices in Using Foam-Type Electrodes for
896 Electrocatalytic Performance Benchmark, *ACS Energy Lett.* 5 (2020) 3260–3264.
897 <https://doi.org/10.1021/acseenergylett.0c01958>.
- 898 [52] J. Van Drunen, B. Kinkead, M.C.P. Wang, E. Sourty, B.D. Gates, G. Jerkiewicz,
899 Comprehensive structural, surface-chemical and electrochemical characterization of
900 nickel-based metallic foams, *ACS Appl. Mater. Interfaces.* 5 (2013) 6712–6722.
901 <https://doi.org/10.1021/am401606n>.
- 902 [53] Y.J. Shih, Z.L. Wu, Y.H. Huang, C.P. Huang, Electrochemical nitrate reduction as
903 affected by the crystal morphology and facet of copper nanoparticles supported on nickel
904 foam electrodes (Cu/Ni), *Chem. Eng. J.* 383 (2020) 123157.
905 <https://doi.org/10.1016/j.cej.2019.123157>.
- 906 [54] F. Jamshidi, W. Kunz, P. Altschuh, T. Lu, M. Laqua, A. August, F. Löffler, M. Selzer,
907 B. Nestler, A 3D computational method for determination of pores per inch (PPI) of
908 porous structures, *Mater. Today Commun.* 34 (2023) 105413.
909 <https://doi.org/10.1016/j.mtcomm.2023.105413>.
- 910 [55] S. Das, N.G. Deen, J.A.M. Kuipers, Multiscale modeling of fixed-bed reactors with
911 porous (open-cell foam) non-spherical particles: Hydrodynamics, *Chem. Eng. J.* 334
912 (2018) 741–759. <https://doi.org/10.1016/j.cej.2017.10.047>.
- 913 [56] I. Mohammed, T. Bauer, M. Schubert, R. Lange, Hydrodynamic multiplicity in a tubular
914 reactor with solid foam packings, *Chem. Eng. J.* 231 (2013) 334–344.
915 <https://doi.org/10.1016/j.cej.2013.07.024>.
- 916 [57] L.F. Arenas, C. Ponce de León, F.C. Walsh, 3D-printed porous electrodes for advanced
917 electrochemical flow reactors: A Ni/stainless steel electrode and its mass transport
918 characteristics, *Electrochem. Commun.* 77 (2017) 133–137.
919 <https://doi.org/10.1016/j.elecom.2017.03.009>.

- 920 [58] A.S. Suleiman, N. Dukhan, Long-domain simulation of flow in open-cell mesoporous
921 metal foam and direct comparison to experiment, *Microporous Mesoporous Mater.* 196
922 (2014) 104–114. <https://doi.org/10.1016/j.micromeso.2014.05.003>.
- 923 [59] F.J. Recio, P. Herrasti, L. Vazquez, C. Ponce De León, F.C. Walsh, Mass transfer to a
924 nanostructured nickel electrodeposit of high surface area in a rectangular flow channel,
925 *Electrochim. Acta.* 90 (2013) 507–513. <https://doi.org/10.1016/j.electacta.2012.11.135>.
- 926 [60] D.F.S. Morais, J.C.B. Lopes, M.M. Dias, V.J.P. Vilar, F.C. Moreira, e-NETmix: A
927 pioneering electrochemical flow reactor with enhanced mass transfer, *Chem. Eng. J.* 481
928 (2024). <https://doi.org/10.1016/j.cej.2023.148244>.
- 929 [61] Z. Qiao, Z. Wang, C. Zhang, S. Yuan, Y. Zhu, J. Wang, PVAm-PIP/PS composite
930 membrane with high performance for CO₂/N₂ separation, *AIChE J.* 59 (2012) 215–228.
931 <https://doi.org/10.1002/aic>.
- 932 [62] W.S. Walker, E. Bezerra Cavalcanti, A. Atrashkevich, A.S. Fajardo, E. Brillas, S.
933 Garcia-Segura, Mass transfer and residence time distribution in an electrochemical cell
934 with an air-diffusion electrode: Effect of air pressure and mesh promoters, *Electrochim.*
935 *Acta.* 378 (2021) 138131. <https://doi.org/10.1016/j.electacta.2021.138131>.
- 936 [63] M.J. Kim, Y. Seo, M.A. Cruz, B.J. Wiley, Metal Nanowire Felt as a Flow-Through
937 Electrode for High-Productivity Electrochemistry, *ACS Nano.* 13 (2019) 6998–7009.
938 <https://doi.org/10.1021/acsnano.9b02058>.
- 939 [64] Y. Chen, G. Zhang, Q. Ji, H. Lan, H. Liu, J. Qu, Visualization of Electrochemically
940 Accessible Sites in Flow-through Mode for Maximizing Available Active Area toward
941 Superior Electrocatalytic Ammonia Oxidation, *Environ. Sci. Technol.* 56 (2022) 9722–
942 9731. <https://doi.org/10.1021/acs.est.2c01707>.
- 943 [65] M.C.O. Monteiro, A. Mirabal, L. Jacobse, K. Doblhoff-Dier, S.C. Barton, M.T.M.
944 Koper, Time-Resolved Local pH Measurements during CO₂Reduction Using Scanning

- 945 Electrochemical Microscopy: Buffering and Tip Effects, *JACS Au*. 1 (2021) 1915–1924.
946 <https://doi.org/10.1021/jacsau.1c00289>.
- 947 [66] M.C.O. Monteiro, M.T.M. Koper, Measuring local pH in electrochemistry, *Curr. Opin.*
948 *Electrochem.* 25 (2021) 100649. <https://doi.org/10.1016/j.coelec.2020.100649>.
- 949 [67] J.H. Han, Exploring the Interface of Porous Cathode/Bipolar Membrane for Mitigation
950 of Inorganic Precipitates in Direct Seawater Electrolysis, *ChemSusChem*. 15 (2022).
951 <https://doi.org/10.1002/cssc.202200372>.
- 952 [68] R. Mao, H. Zhu, K.F. Wang, X. Zhao, Selective conversion of nitrate to nitrogen gas by
953 enhanced electrochemical process assisted by reductive Fe(II)-Fe(III) hydroxides at
954 cathode surface, *Appl. Catal. B Environ.* 298 (2021) 120552.
955 <https://doi.org/10.1016/j.apcatb.2021.120552>.
- 956 [69] M.D. Patil, S.D. Dhas, A.A. Mane, A. V. Moholkar, Clinker-like V₂O₅ nanostructures
957 anchored on 3D Ni-foam for supercapacitor application, *Mater. Sci. Semicond. Process.*
958 133 (2021) 105978. <https://doi.org/10.1016/j.mssp.2021.105978>.
- 959 [70] M. Thommes, K. Kaneko, A. V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J.
960 Rouquerol, K.S.W. Sing, Physisorption of gases, with special reference to the evaluation
961 of surface area and pore size distribution (IUPAC Technical Report), *Pure Appl. Chem.*
962 87 (2015) 1051–1069. <https://doi.org/10.1515/pac-2014-1117>.
- 963 [71] E. Gregorová, T. Uhlířová, W. Pabst, P. Diblíková, I. Sedlářová, Microstructure
964 characterization of mullite foam by image analysis, mercury porosimetry and X-ray
965 computed microtomography, *Ceram. Int.* 44 (2018) 12315–12328.
966 <https://doi.org/10.1016/j.ceramint.2018.04.019>.
- 967 [72] S. Trasatti, O.A. Petrii, International Union of Pure and Applied Chemistry Physical
968 Chemistry Division Commission on Electrochemistry: Real Surface Area Measurements
969 in Electrochemistry, *Pure Appl. Chem.* 63 (1991) 711–734.

970 <https://doi.org/10.1351/pac199163050711>.

971 [73] A. Lasia, A. Rami, Kinetics of hydrogen evolution on nickel electrodes, *J. Electroanal.*
972 *Chem.* 294 (1990) 123–141. [https://doi.org/10.1016/0022-0728\(90\)87140-F](https://doi.org/10.1016/0022-0728(90)87140-F).

973 [74] T.R.L.C. Paixão, Measuring Electrochemical Surface Area of Nanomaterials versus the
974 Randles–Ševčík Equation, *ChemElectroChem.* 7 (2020) 3414–3415.
975 <https://doi.org/10.1002/celec.202000633>.

976 [75] P. Connor, J. Schuch, B. Kaiser, W. Jaegermann, The Determination of Electrochemical
977 Active Surface Area and Specific Capacity Revisited for the System MnO_x as an
978 Oxygen Evolution Catalyst, *Zeitschrift Fur Phys. Chemie.* 234 (2020) 979–994.
979 <https://doi.org/10.1515/zpch-2019-1514>.

980 [76] C. Hurth, C. Li, A.J. Bard, Direct probing of electrical double layers by scanning
981 electrochemical potential microscopy, *J. Phys. Chem. C.* 111 (2007) 4620–4627.
982 <https://doi.org/10.1021/jp0661084>.

983 [77] A.J. Bard, L.R. Faulkner, *Fundamentals and Applications Plasmonics : Fundamentals*
984 *and Applications*, 2nd ed., John Wiley & Sons, Inc., 2001.

985 [78] O. Gharbi, M.T.T. Tran, M.E. Orazem, B. Tribollet, M. Turmine, V. Vivier, Impedance
986 Response of a Thin Film on an Electrode: Deciphering the Influence of the Double Layer
987 Capacitance, *ChemPhysChem.* 22 (2021) 1371–1378.
988 <https://doi.org/10.1002/cphc.202100177>.

989 [79] D.M. Morales, M. Risch, Seven steps to reliable cyclic voltammetry measurements for
990 the determination of double layer capacitance, *JPhys Energy.* 3 (2021) 034013.
991 <https://doi.org/10.1088/2515-7655/abee33>.

992 [80] S. Akkari, V. Vivier, C.M. Sánchez-Sánchez, Urea electro-oxidation byproducts impact
993 on NiO/NiOOH anode performance studied by operando electrochemical impedance
994 spectroscopy, *Electrochim. Acta.* 474 (2024) 143526.

- 995 <https://doi.org/10.1016/j.electacta.2023.143526>.
- 996 [81] G.J. Brug, A.L.G. van den Eeden, M. Sluyters-Rehbach, J.H. Sluyters, The analysis of
997 electrode impedances complicated by the presence of a constant phase element, *J.*
998 *Electroanal. Chem.* 176 (1984) 275–295. [https://doi.org/10.1016/S0022-0728\(84\)80324-](https://doi.org/10.1016/S0022-0728(84)80324-1)
999 1.
- 1000 [82] O. Gharbi, M.T.T. Tran, B. Tribollet, M. Turmine, V. Vivier, Revisiting cyclic
1001 voltammetry and electrochemical impedance spectroscopy analysis for capacitance
1002 measurements, *Electrochim. Acta.* 343 (2020) 136109.
1003 <https://doi.org/10.1016/j.electacta.2020.136109>.
- 1004 [83] S.P. Zankowski, P.M. Vereecken, Electrochemical Determination of Porosity and
1005 Surface Area of Thin Films of Interconnected Nickel Nanowires, *J. Electrochem. Soc.*
1006 166 (2019) D227–D235. <https://doi.org/10.1149/2.0311906jes>.
- 1007 [84] U.S.G. Survey, Rare Earth Elements — Critical Resources for High Technology, (2002)
1008 1–11.
- 1009 [85] X. Lu, H. Song, J. Cai, S. Lu, Recent development of electrochemical nitrate reduction
1010 to ammonia: A mini review, *Electrochem. Commun.* 129 (2021) 107094.
1011 <https://doi.org/10.1016/j.elecom.2021.107094>.
- 1012 [86] J. Gao, B. Jiang, C. Ni, Y. Qi, X. Bi, Enhanced reduction of nitrate by noble metal-free
1013 electrocatalysis on P doped three-dimensional Co₃O₄ cathode: Mechanism exploration
1014 from both experimental and DFT studies, *Chem. Eng. J.* 382 (2020) 123034.
1015 <https://doi.org/10.1016/j.cej.2019.123034>.
- 1016 [87] Y. Wang, C. Wang, M. Li, Y. Yu, B. Zhang, Nitrate electroreduction: Mechanism
1017 insight, In situ characterization, performance evaluation, and challenges, *Chem. Soc.*
1018 *Rev.* 50 (2021) 6720–6733. <https://doi.org/10.1039/d1cs00116g>.
- 1019 [88] X. bo Li, G. ri Xu, Hydrothermal vs electrodeposition: How does deposition method

- 1020 affect the electrochemical capacitor performance of manganese dioxide?, *Ceram. Int.* 43
1021 (2017) 8963–8969. <https://doi.org/10.1016/j.ceramint.2017.04.036>.
- 1022 [89] D. Taherinia, M. Moazzeni, S. Moravej, Comparison of hydrothermal and
1023 electrodeposition methods for the synthesis of CoSe₂/CeO₂ nanocomposites as
1024 electrocatalysts toward oxygen evolution reaction, *Int. J. Hydrogen Energy.* 47 (2022)
1025 17650–17661. <https://doi.org/10.1016/j.ijhydene.2022.03.257>.
- 1026 [90] G.A. Cerrón-Calle, A. Maya, D. Leon, M. Roldan, A.S. Fajardo, C.M. Sánchez-Sánchez,
1027 S. Garcia-Segura, Unlocking Sustainable Nitrate Reduction: Earth-Abundant Bimetallic
1028 Electrodes Under Galvanostatic Evaluation, *Electrochim. Acta.* (2024) 144263.
1029 <https://doi.org/10.1016/j.electacta.2024.144263>.
- 1030 [91] Y. Xu, Y. Sheng, M. Wang, T. Ren, K. Shi, Z. Wang, X. Li, L. Wang, H. Wang,
1031 Interface coupling induced built-in electric fields boost electrochemical nitrate reduction
1032 to ammonia over CuO@MnO₂ core-shell hierarchical nanoarrays, *J. Mater. Chem. A.* 10
1033 (2022) 16883–16890. <https://doi.org/10.1039/d2ta02006h>.
- 1034 [92] C. Zhou, J. Bai, Y. Zhang, J. Li, Z. Li, P. Jiang, F. Fang, M. Zhou, X. Mei, B. Zhou,
1035 Novel 3D Pd-Cu(OH)₂/CF cathode for rapid reduction of nitrate-N and simultaneous
1036 total nitrogen removal from wastewater, *J. Hazard. Mater.* 401 (2021) 123232.
1037 <https://doi.org/10.1016/j.jhazmat.2020.123232>.
- 1038 [93] X. Wang, M. Zhu, G. Zeng, X. Liu, C. Fang, C. Li, A three-dimensional Cu nanobelt
1039 cathode for highly efficient electrocatalytic nitrate reduction, *Nanoscale.* 12 (2020)
1040 9385–9391. <https://doi.org/10.1039/c9nr10743f>.
- 1041 [94] Y. Zhang, Y. Zhao, Z. Chen, L. Wang, L. Zhou, P. Wu, F. Wang, P. Ou, Fe/Cu
1042 Composite Electrode Prepared by Electrodeposition and Its Excellent Behavior in Nitrate
1043 Electrochemical Removal, *J. Electrochem. Soc.* 165 (2018) E420–E428.
1044 <https://doi.org/10.1149/2.0081810jes>.

- 1045 [95] W. Fu, Y. Du, J. Jing, C. Fu, M. Zhou, Highly selective nitrate reduction to ammonia on
1046 CoO/Cu foam via constructing interfacial electric field to tune adsorption of reactants,
1047 Appl. Catal. B Environ. 324 (2023) 122201.
1048 <https://doi.org/10.1016/j.apcatb.2022.122201>.
- 1049 [96] F. Yao, M. Jia, Q. Yang, F. Chen, Y. Zhong, S. Chen, L. He, Z. Pi, K. Hou, D. Wang, X.
1050 Li, Highly selective electrochemical nitrate reduction using copper phosphide self-
1051 supported copper foam electrode: Performance, mechanism, and application, Water Res.
1052 193 (2021). <https://doi.org/10.1016/j.watres.2021.116881>.
- 1053 [97] X. Tan, X. Wang, T. Zhou, T. Chen, Y. Liu, C. Ma, H. Guo, B. Li, Preparation of three
1054 dimensional bimetallic Cu–Ni/NiF electrodes for efficient electrochemical removal of
1055 nitrate nitrogen, Chemosphere. 295 (2022) 133929.
1056 <https://doi.org/10.1016/j.chemosphere.2022.133929>.
- 1057 [98] S. Zhang, M. Li, J. Li, Q. Song, X. Liu, High-ammonia selective metal – organic
1058 framework – derived Co-doped Fe / Fe₂O₃ catalysts for electrochemical nitrate
1059 reduction, 119 (2022) 2115504119.
1060 <https://doi.org/https://doi.org/10.1073/pnas.2115504119>.
- 1061 [99] J. Wang, J. Feng, T.O. Soyol-Erdene, Z. Wei, W. Tang, Electrodeposited NiCoP on
1062 nickel foam as a self-supported cathode for highly selective electrochemical reduction of
1063 nitrate to ammonia, Sep. Purif. Technol. 320 (2023) 124155.
1064 <https://doi.org/10.1016/j.seppur.2023.124155>.
- 1065 [100] Y. Gao, R. Wang, Y. Li, E. Han, M. Song, Z. Yang, F. Guo, Y. He, X. Yang, Regulating
1066 dynamic equilibrium of active hydrogen for super-efficient nitrate electroreduction to
1067 ammonia, Chem. Eng. J. 474 (2023) 145546. <https://doi.org/10.1016/j.cej.2023.145546>.
- 1068 [101] W. Tao, P. Wang, B. Hu, X. Wang, G. Zhou, Accelerating the reaction kinetics from
1069 nitrate to ammonia by anion substitution in NiCo-based catalysts, J. Environ. Chem.
1070 Eng. 11 (2023) 109117. <https://doi.org/10.1016/j.jece.2022.109117>.

- 1071 [102] Z.H. Xue, H.C. Shen, P. Chen, G.X. Pan, W.W. Zhang, W.M. Zhang, S.N. Zhang, X.H.
1072 Li, C.T. Yavuz, Boronization of Nickel Foam for Sustainable Electrochemical Reduction
1073 of Nitrate to Ammonia, *ACS Energy Lett.* (2023) 3843–3851.
1074 <https://doi.org/10.1021/acsenergylett.3c01139>.
- 1075 [103] Y. Wang, S. Shu, M. Peng, L. Hu, X. Lv, Y. Shen, H. Gong, G. Jiang, Dual-site
1076 electrocatalytic nitrate reduction to ammonia on oxygen vacancy-enriched and Pd-
1077 decorated MnO₂ nanosheets, *Nanoscale*. 13 (2021) 17504–17511.
1078 <https://doi.org/10.1039/d1nr04962c>.
- 1079 [104] F. Li, Y.C. Li, Z. Wang, J. Li, D.-H. Nam, Y. Lum, M. Luo, X. Wang, A. Ozden, S.-F.
1080 Hung, B. Chen, Y. Wang, J. Wicks, Y. Xu, Y. Li, C.M. Gabardo, C.-T. Dinh, Y. Wang,
1081 T.-T. Zhuang, D. Sinton, E.H. Sargent, Cooperative CO₂-to-ethanol conversion via
1082 enriched intermediates at molecule–metal catalyst interfaces, *Nat. Catal.* 3 (2020) 75–82.
1083 <https://doi.org/10.1038/s41929-019-0383-7>.
- 1084 [105] E. Vichou, A. Solé-Daura, C. Mellot-Draznieks, Y. Li, M. Gomez-Mingot, M.
1085 Fontecave, C.M. Sánchez-Sánchez, Electrocatalytic Conversion of CO₂ to Formate at
1086 Low Overpotential by Electrolyte Engineering in Model Molecular Catalysis,
1087 *ChemSusChem*. 15 (2022) 1–10. <https://doi.org/10.1002/cssc.202201566>.
1088